CHEMISTRY LETTERS, pp. 301-302, 1977. Published by the Chemical Society of Japan

REACTIONS OF ALLYLTIN COMPOUNDS III[1)]
ALLYLATION OF AROMATIC HALIDES WITH ALLYLTRIBUTYLTIN IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

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Catalytic allylation of aryl halides with allyltributyltin in the presence of tetrakis(triphenylphosphine)palladium(0) was investigated. The reaction with aryl bromides proceeded efficiently to yield allylbenzenes.

Allyl derivatives of aromatic compounds are readily obtained by the reaction of aromatic Grignard reagents or lithium compounds with allylic halides. The reaction is limited, however, because substituents such as nitro, carbonyl groups etc, which are sensitive to these reagents can not be present. Recently Heck reported that aryl palladium salts, prepared in situ from arylmercuric salts and palladium(II) compounds, react with allylic halides at room temperature to produce allylaromatic derivatives.[2)]

$$\mathrm{ArHgX} + \mathrm{PdX_2} \rightleftharpoons [\mathrm{ArPdX}] + \mathrm{HgX_2}$$

$$[\mathrm{ArPdX}] + \mathrm{CH_2{=}CHCH_2X} \rightleftharpoons [\mathrm{ArCH_2CH(PdX)CH_2X}]$$

$$[\mathrm{ArCH_2CH(PdX)CH_2X}] \longrightarrow \mathrm{ArCH_2CH{=}CH_2} + \mathrm{PdX_2}$$

We wish to report novel catalytic allylation of aromatic halides with allyltributyltin in the presence of tetrakis(triphenylphosphine)palladium(0).

$$\mathrm{ArX} + \mathrm{Pd(0)} \longrightarrow [\mathrm{ArPdX}]$$

$$[\mathrm{ArPdX}] + \mathrm{CH_2{=}CHCH_2SnBu_3} \longrightarrow \mathrm{ArCH_2CH{=}CH_2} + \mathrm{XSnBu_3} + \mathrm{Pd(0)}$$

The following example demonstrates the simplicity and efficiency of the present process and illustrates the typical procedure: after 0.314g (2 mmol) of bromobenzene and 0.695g (2.1 mmol) of allyltributyltin were allowed to react with 0.023g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0) in 1 ml of benzene

TABLE The Reaction of Aromatic Halides with Allyltributyltin

Substrate				Conditions		Conversiton	Yield* of
Ar-X		Allyl-$SnBu_3$	Catalyst	Temp.	Time	of Ar-X	$ArCH_2CH=CH_2$
C_6H_5Cl	2 mmol	2.2 mmol	0.02 mmol	120°	20 hr	0 %	0 %
p-ClC_6H_4Cl	2	2.2	0.02	120	20	10	4
p-$NO_2C_6H_4Cl$	2	2.2	0.02	120	20	100	59
C_6H_5Br	2	2.1	0.02	100	20	100	96
p-ClC_6H_4Br	2	2.2	0.02	100	20	100	100
p-$CH_3OC_6H_4Br$	2	2.2	0.02	120	20	100	96
p-$CH_3COC_6H_4Br$	2	2.2	0.02	100	20	100	98
p-$NO_2C_6H_4Br$	2	2.2	0.02	100	20	100	72
C_6H_5I	2	2.2	0.02	80	20	46	32
	2	2.2	0.02	120	20	79	24
p-ClC_6H_4I	2	2.2	0.02	80	20	27	25
	2	2.2	0.02	120	20	41	29

* Based on the aryl halide.

in a sealed tube at 100°C for 20 hours, the resulting mixture was subjected to glpc, and allylbenzene was obtained in 96% yield based on the bromobenzene. The structure of the product was determined by spectroscopic analysis. The results of the reaction are listed in the Table.

The reactions are thought to proceed via oxidative addition of aryl halides to the palladium(0). As Table shows, aryl bromide is the best substrate of aryl halides, affording the corresponding allylbenzene in high yield, and negative substituents seem to enhance the reactivity of aryl chloride. These tendencies may be explained in terms of the reactivities of aryl halides in oxidative addition to the palladium catalyst[3] and the nature of the oxidative adducts; aryl chloride is least reactive towards the palladium(0) and the adduct of aryl iodide to the catalyst might collapse, partly, in the manner which does not regenerate the palladium(0).

REFERENCE

1) Part II; M. Kosugi, Y. Shimizu and T. Migita, J. Organometal. Chem., in press.
2) R. F. Heck, J. Am. Chem. Soc., 90, 5531, (1968).
R. F. Heck, ibid, 90, 5518, (1968).
3) P. Fitton and E. A. Rick, J. Organometal. Chem., 28, 287, (1971).

(Received January 27, 1977)