Journal of Organometallic Chemistry, 91 (1975) C39—C42

Preliminary communication

THE REACTION OF σ-VINYLPALLADIUM COMPLEXES WITH ALKYLLITHIUMS. STEREOSPECIFIC SYNTHESES OF OLEFINS FROM VINYL HALIDES AND ALKYLLITHIUMS

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(Received March 3rd, 1975)

Summary

Vinyl halides react with alkyllithium compounds in the presence of tetrakis(triphenylphosphine)palladium to give olefins stereospecifically in excellent or fairly good yields. When less reactive Grignard reagents are employed instead of alkyllithium compounds, these reactions can be carried out catalytically with palladium.

Recently we reported a convenient method for selective *ortho*-alkylation of benzaldehydes and related compounds. Thus, the σ-aryl chelate complexes derived by palladation of Schiff bases and related compounds can be readily treated with alkyllithium compounds in the presence of triphenylphosphine to give *ortho*-alkylated compounds via the intermediacy of aryl—alkylpalladium complexes [1].

The oxidative addition of alkyl halides to low valent transition metal complexes is a subject of much current interest [2]. Vinyl halides have been demonstrated to add oxidatively to palladium(0)* and platinum(0) complexes [4] with retention of configuration. Extension of the above reaction of σ-arylpalladium complexes with alkyllithiums to vinylpalladium complexes would provide a new method for selective syntheses of olefins. It is known that reaction of a vinyl halide with tetrakis(triphenylphosphine)palladium (I) in benzene gives a σ-vinylpalladium complex [3]. We have found that these can be treated with a molar equivalent of alkyllithium compound to give an olefin in excellent or fairly good yields. Thus, (*E*)-bromostyrene can be converted into (*E*)-propenylbenzene in 98 % yield with complete retention of stereochemistry. Similarly, (*Z*)-bromostyrene gives (*Z*)-propenylbenzene in a stereospecific manner (the content of the (*E*)-isomer is less than 1 %) in 88 % yield.

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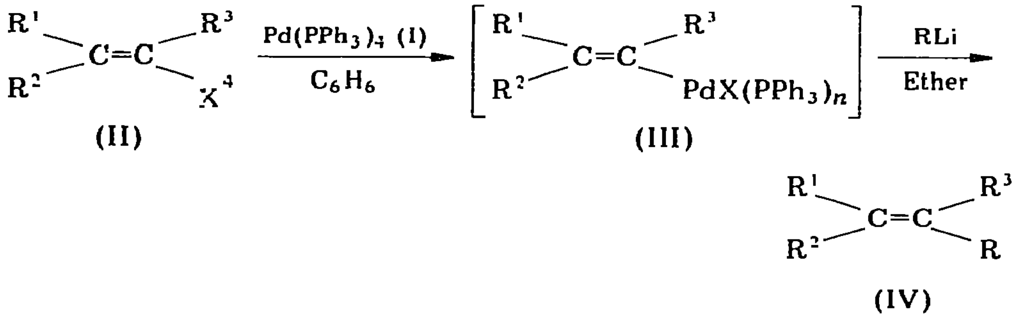
* 1,2-Dichloroethylene add to $Pd(PPh_3)_{4-n}$ with retention of configuration [3].

TABLE 1

THE REACTIONS OF VINYL HALIDES, II, WITH EITHER ALKYLLITHIUM COMPOUNDS OR GRIGNARD REAGENTS INDUCED BY PALLADIUM COMPLEX I

Halides II				RLi (RMgX')	Yields [a] of IV (%)	Isomeric purity [b]
R^1	R^2	R^3	X			
H	Ph	H	Br	CH_3Li	88	99
H	Ph	H	Br	$n\text{-}C_4H_9Li$	66	99
H	Ph	H	Br	$p\text{-}CH_3C_6H_4Li$	98	99
Ph	H	H	Br	CH_3Li	98	100
Ph	H	H	Br	CH_3MgI	99	100
Ph	H	H	Br	$n\text{-}C_4H_9Li$	55	100
Ph	H	H	Br	$p\text{-}CH_3C_6H_4Li$	98	99
Ph	H	H	Br	$CH_2{=}CHMgBr$	91	99.5
H	Ph	H	Cl	CH_3Li	90	100
H	Ph	H	Cl	$p\text{-}CH_3C_6H_4Li$	92	100
H	$n\text{-}C_4H_9$	H	Br	$n\text{-}C_4H_9Li$	63 [c]	99.5
H	$n\text{-}C_4H_9$	H	Br	$p\text{-}CH_3C_6H_4Li$	81 [c]	99
Ph	CH_3	H	Br	CH_3Li	89 [c]	99

[a] All yields are based on relative GLC peak areas, corrected for the sensitivity of the detector, using mainly naphthalene as reference. [b] The isomeric purity was determined by relative GLC areas with those of the corresponding stereoisomers. [c] Oxidative addition was carried out in refluxing benzene for 3 h, but the halide was still recovered in 10-20% yield.

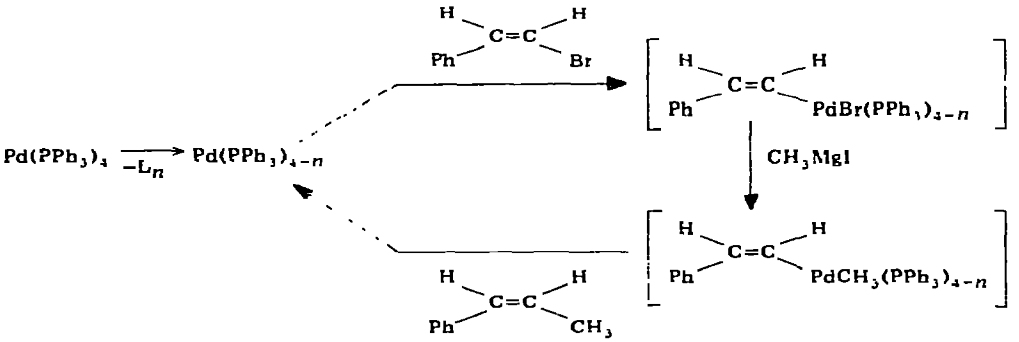


A typical procedure is as follows. To a 50 ml round-bottomed flask containing I (1 mmol) was added a solution of (*E*)-bromostyrene (1 mmol) in benzene (10 ml) under argon. The mixture was stirred at ambient temperature for 2 h. The color of the suspension changed from green-yellow to white-yellow. To the mixture was added a solution of methyllithium (1 mmol) in ether (5 ml) for 10 min. After additional stirring for 50 min, the precipitated materials were filtered off and washed with ether (20 ml). The ethereal solution was washed with water and dried. Distillation gave (*E*)-propenylbenzene in 85% yield. Careful GLC analysis indicated that the (*E*)-isomer was not contaminated with the (*Z*)-isomer.

The other examples of stereoselective syntheses of di- and tri-substituted olefins are summarized in Table 1. Products were analyzed by gas chromatography, isolated, and characterized by comparison with authentic samples. Because of its high yields and extremely high stereoselectivity, this reaction may be useful for the synthesis of olefins, although stereoselective cross coupling of olefinic halides with either Grignard reagents in the presence of nickel phosphine complexes [5] and iron(III) chloride [6] or with lithium dialkylcuprates [7] have been reported.

It should be noted that alkyllithium in the absence of $(Ph_3P)_4Pd$ is a totally unsatisfactory reagent for these coupling reactions. The reaction of methyllithium with bromostyrene produces phenylacetylene mainly. Therefore, this palladium-induced carbon—carbon bond formation cannot be carried out catalytically, since recycling of the palladium catalyst is slower than metallation of vinyl halide by the alkyllithium, resulting in formation of an acetylenic compound. However, when less reactive Grignard reagents are utilized, the anticipated catalytic reaction which may be envisioned by Scheme 1 can be accomplished. Treatment of (*Z*)-bromostyrene (1.0 mmol) with I (0.029 mmol) and methylmagnesium iodide (3.0 mmol) in benzene (10 ml) gave 1.0 mmol of (*Z*)-propenylbenzene (3400 % yield based in palladium) (isomeric purity 99 %). Similarly, (*E*)-bromostyrene can be converted to (*E*)-propenylbenzene (3440 % yield based on palladium), (*E*)-1-phenylbutadiene (2800 %), and (*E*)-1-phenyl-2-(4′-methylphenyl)ethylene (2950 %) with retention of configuration on treatment with methylmagnesium iodide, vinylmagnesium bromide, and *p*-tolylmagnesium bromide, respectively under the same reaction conditions.

SCHEME 1



The fact that σ-vinylpalladium complexes, III, derived from vinyl halides, II, and I react with alkyllithium compounds with retention of configuration at the olefinic double bond indicates that the addition of $Pd(PPh_3)_{4-n}$ to vinyl halides proceeds with retention of configuration. This stereochemical result is sufficient to establish that free radicals are not involved in these reactions because of the known facile inversion of configuration of vinyl radicals [8].

References

1 S.-I. Murahashi, Y. Tanba, M. Yamamura and I. Moritani, Tetrahedron Lett., (1974) 3749.
2 (a) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, J. Amer. Chem. Soc., 95 (1973) 3180,
  (b) M.F. Lappert and P.W. Lender, Chem. Commun., (1973) 948;
  (c) J.P. Collman and M.R. MacLaury; J. Amer. Chem. Soc., 96 (1974) 3019;
  (d) P.K. Wong, K.S. Lau and J.K. Stil, J. Amer. Chem. Soc., 96 (1974) 5956;
  (e) A.V. Kramer, J A. Labinger, J.S. Bradley and J.A. Osborn, J. Amer. Chem. Soc., 96 (1974) 7145.
3 P. Fitton and J.E. McKeon, Chem. Commun., (1968) 4.
4 (a) J. Rajaran, R.G. Pearson and J.A. Ibers, J. Amer. Chem. Soc., 96 (1974) 2103;
  (b) B.E. Mann, B.L. Shaw and N.I. Tucker, J. Chem. Soc. A, (1971) 2667.

5 (a) K. Tamao, K. Sumitani and M. Kumada, J. Amer. Chem. Soc., 94 (1972) 4374;
(b) K. Tamao, M. Zenbayashi, Y. Kiso and M. Kumada, J. Organometal. Chem., 55 (1973) C91;
(c) J.P. Corriu and J.P. Masse, Chem. Commun., (1972) 144.
6 M. Tamura and J.K. Kochi, J. Amer. Chem. Soc., 93 (1971) 1487; Syntheses, (1971) 303.
7 E.J. Corey and G.H. Posner, J. Amer. Chem. Soc., 89 (1967) 3912; 90 (1968) 5616.
8 (a) O. Shimamura, K. Tokumaru and H. Yui, Tetrahedron Lett., (1966) 5141;
(b) J.A. Kampmeier and R.M. Fantzier, J. Amer. Chem. Soc., 88 (1968) 1959;
(c) G.M. Whitesides, C.P. Casey and J.K. Krieger, J. Amer. Chem. Soc., 93 (1971) 1379.