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Palladium Catalyzed Reactions of Organic Halides with Organotin Compounds Involving Insertion of Norbornene. Synthesis of 2,3-Disubstituted Norbornane

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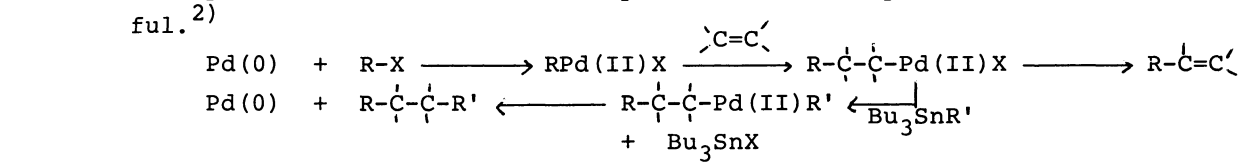
2,3-Disubstituted norbornenes were prepared by the palladium catalyzed reaction of a ternary system composed of organic halide, organotin compound, and norbornene. Aryl and vinyl bromides, and acyl chloride were good substrates, but benzyl and allyl chlorides were not. Vinyl, phenyl, ethynyl, and allyltin compounds were utilizable reagents.

The combination between a Heck type reaction[1] and a Pd-catalyzed cross-coupling reaction of organic halides with organotins, that is, cross-coupling involving insertion of olefin, is expected to be a short-cut procedure for building up the complex molecule directly. Unfortunately, the fast β-elimination of the palladation product between olefin and palladium(II) complex makes this method unsuccessful.[2]



In 1982, Chiusoli et al. reported one-pot synthesis of 2,3-disubstituted norbornane by the reaction of vinyl bromides, terminal acetylene, and norbornene in the presence of a palladium complex.[3] More recently, Larlock et al. reported that norbornene was the best olefin which was inserted into a palladium(II) complex and the adduct was not suffered from the β-elimination.[4]

In this letter, we report the palladium catalyzed reaction of organic halides with organotin compounds involving the insertion of norbornene.

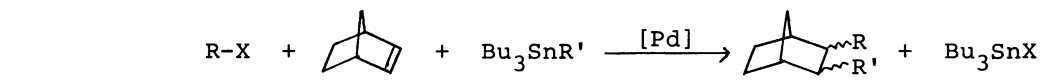
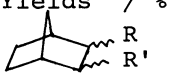


Table 1 shows the results giving the products as be intended. Especially the system of aryl or vinylic bromide and vinyltin gave the products in good yields, irrespective of the nature of the substituent in aryl bromide. Benzoyl chloride also gave the product in rather low yield accompanied by phenyl vinyl ketone, the direct coupling product. However, the expected product could not be formed in the case of the reaction with benzyl or allyl chloride. The reaction with 1-alkynyltin and bromobenzene gave the direct coupling product rather than expected one.

Table 1. Pd-Catalyzed reaction of organic halides and norbornene with organotin compounds[a)]

R-X	Bu_3SnR' -R'	Temp °C	Time h	Yields[b)] / % of  [c)] and R-R'	
PhBr	$-CH=CH_2$	100	10	87	
p-MeC_6H_4Br	$-CH=CH_2$	100	10	(95)	
p-AcC_6H_4Br	$-CH=CH_2$	100	10	(96)	
PhCH=CHBr (E)	$-CH=CH_2$	100	10	(91)	
CH_2=CHBr	$-CH=CH_2$	100	10	64	
PhCOCl	$-CH=CH_2$	80	12	(36)	(39)
PhBr	$-C\equiv CPh$	100	12	28	(44)
PhI	$-C\equiv CPh$	60	12	(56)	(7)
PhCH=CHBr (E)	$-C\equiv CPh$	100	12	64	(7)
PhBr	-Ph	100	20	60	(10)
PhCH=CHBr (E)	-Ph	100	20	71	(6)
PhBr	$-CH_2CH=CH_2$	100	20	47	(9)
PhBr	$-CH_2CH=CH_2$	80	48	(49)	(5)
PhCH=CHBr (E)	$-CH_2CH=CH_2$	80	48	(36)	(19)

a) Organic halide(1 mmol), norbornene (2 mmol), organotin compound (1 mmol), and $Pd(PPh_3)_4$ (0.01 mmol) in benzene (1 cm^3) were used. b) Isolated yield based on the halide, in parenthesis GLC yield. c) Although the exact stereochmistry was not determined, spectroscopic data of some products were consitent with that of exo, cis form reported.[3)]

The yield of latter was improved by the use of iodobenzene in place of bromobenzene at lower temperature. Moderate yields of the products were obtained in the reaction with phenyltin compound. However, the reaction with allyltin compound gave the products in rather low yields.

Although the reaction conditions are not optimized at present, these reactions seem to open the new methodology for the preparation of the 2,3-disubstituted norbornanes.

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References

1) R. F. Heck, Pure Appl. Chem., 50, 691 (1978).
2) L. S. Hegedus, Tetrahedron, 40, 2415 (1984) and references cited therein.
3) M. Catellani and G. P. Chiusoli, Tetrahedron Lett., 23, 4517 (1982).
4) R. C. Larock, S. S. Hershberger, K. Takagi, and M. A. Mitchell, J. Org. Chem., 51, 2450 (1986).

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