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PALLADIUM-CATALYZED SYNTHESIS OF ALLENES.

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Summary : Substituted allenes are selectively obtained in good yields from the reaction of Grignard reagents with propargylic or allenic halides in the presence of catalytic amounts of palladium chloride, triphenylphosphine and diisobutyl aluminum hydride, in tetrahydrofuran at room temperature.

Palladium catalysis plays an important role in organic synthesis [1]. In particular, cross-coupling reactions between Grignard reagents and aryl [2] or vinyl [3] halides are efficiently catalyzed by palladium complexes.

We wish to report a Pd-promoted synthesis of substituted allenes from the reaction of propargylic or allenic halides with Grignard reagents.
Indeed, fair to good yields of (3) have been obtained when Grignard reagents were added to (1) or (2) in the presence of catalytic amounts of palladium chloride, triphenylphosphine and diisobutylaluminum hydride in tetrahydrofuran, at room temperature (Table).

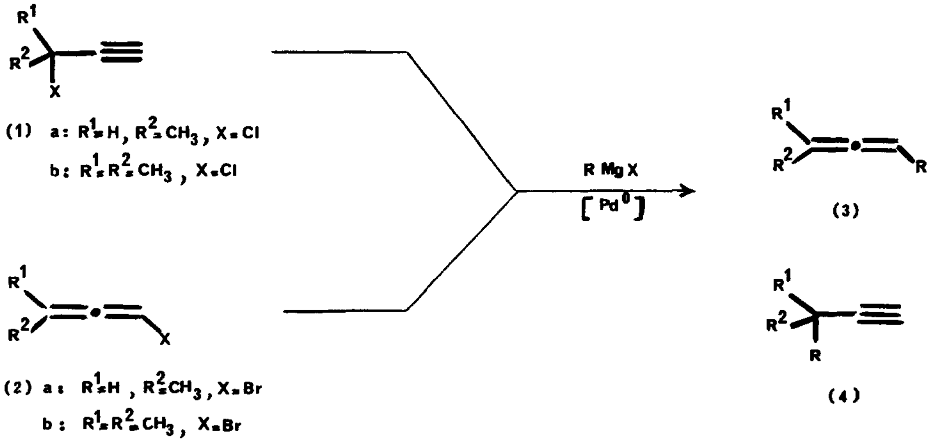

Table : Pd-catalyzed [a] cross-coupling reaction of propargylic and allenic halides with Grignard reagents (solvent : THF ; reaction time : 1h ; t°=25°C).

Substrate	RMgX	Total yield[b] (%) (3) + (4)	%(3)
1a	$C_8H_{17}MgCl$[c]	62	99
1a	$CH_3C_6H_4MgBr$	67	99
2a	$C_8H_{17}MgCl$[d]	60	90
2a	$CH_3C_6H_4MgBr$	48[e]	93
1b	$C_8H_{17}MgCl$	77[e]	99
1b	$CH_3C_6H_4MgBr$	75[e]	99
2b	$C_8H_{17}MgCl$	98	99
2b	$CH_3C_6H_4MgBr$	67[e]	99

a) Substrate : RMgX : $PdCl_2$: PPh_3 : $AlH(iBu)_2$ = 1 : 1.4 : 0.1 : 0.2 : 0.1 ; b) GLC yield unless otherwise noted ; c) In the same reaction conditions but without Pd catalyst, a mixture (72:28) of (3) : (4) was obtained in 34 % yield ; d) In the same reaction conditions but without Pd catalyst, a mixture (37 : 63) of (3) : (4) was obtained in 38 % yield ; e) isolated product.

From the results it seems that the degree of substitution of the halides has a greater influence on the reaction yields than the nature of the unsaturated functional group better yields are obtained with more substituted halides whether they are propargylic or allenic. The reaction very probably proceeds through the formation of allenic Pd complexes from both acetylenic or allenic halides by oxidative addition of (1) or (2) to Pd $(PPh_3)_x$ formed in situ by reduction of palladium chloride followed by cross-coupling with Grignard reagents.

Further applications of allenic Pd intermediates in organic synthesis are currently being investigated.

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References.

1 J. Tsuji, "Organic Synthesis with Palladium Compounds", Springer-Verlag, Berlin Heidelberg, New-York, 1980.

2 a) J.F. Fauvarque and A. Jutand, Bull. Soc. Chim. Fr., 1976, 765 ; b) A. Sekiya and N. Ishikawa, J. Organometal. Chem. 1976, 118, 349.

3 a) M. Yamamura, I. Moritani and S.I. Murahashi, J. Organometal. Chem., 1975, 91, C 39 ; b) S.I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita and K. Kondo, J. Org. Chem., 1979, 44, 2408. c) H.P. Dang and G. Linstrumelle, Tetrahedron Letters, 1978, 191.

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