Palladium-Catalyzed Arylation and Vinylation of Allenyllithium Reagents; A Route to Arylallenes, 1,2,4-Alkatrienes, and 1-Alkenyl Ketones

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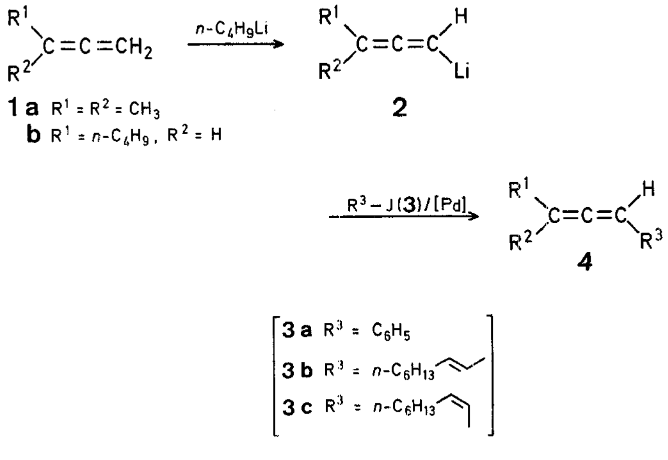
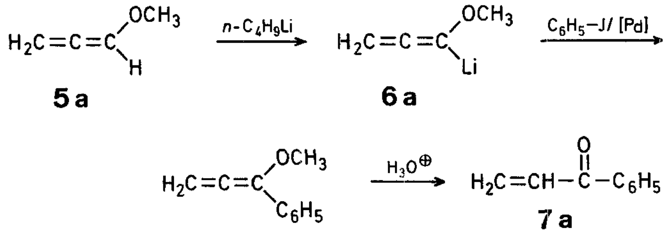
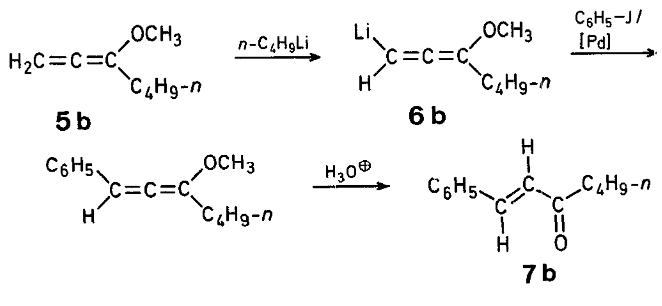
Nucleophilic substitution of aryl[1,2] and vinyl halides[3,4,5] by organomagnesium and organolithium reagents occurs readily in the presence of catalytic amounts of zerovalent palladium complexes. We have recently shown that this type of reaction can be extended to propargylic and allenic halides, thus providing a synthesis of substituted allenes[6]. We report herein an alternative route to this type of compounds. Since allenyllithium compounds are readily available from the metallation of allenes by butyllithium[7,8], a successful cross-coupling between allenyllithium compounds **(2)** and aryl or vinyl halides **(3)** should provide a convenient route to arylallenes or 1,2,4-alkatrienes, **(4)**, respectively. The results obtained (Table 1) show that these compounds are obtained in good yields when aryl or vinyl halides **(3)** are treated with allenyllithium compounds **(2)** in the presence of a palladium catalyst in tetrahydrofuran at room temperature under an argon atmosphere. The palladium catalyst can be used as preformed tetrakis[triphenylphosphine]-palladium or may be formed *in situ* from palladium chloride, triphenylphosphine, and diisobutylaluminium hydride.



Since 1-methoxyallenes are efficient precursors of 1-alkenyl ketones[9], the analogous reaction of 1-methoxyallenes **(5)** may be used for the preparation of 1-alkenyl ketones **(7)**. Depending on the nature of the 1-methoxyallene (**5**; H or alkyl at the 1-position), the lithiation-arylation sequence via **6a** or **6b** affords phenyl vinyl ketones **(7a)** or alkyl styryl ketones **(7b)**, respectively.





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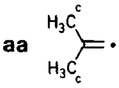
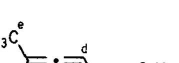
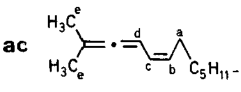
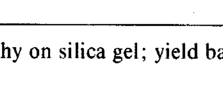
1-Phenyl-1,2-heptadiene (4ba); Typical Procedure:

A solution of 1,2-heptadienyllithium[7] **(2b)** is freshly prepared at −70 °C from 1,2-heptadiene (**1b**; 0.73 g, 7.65 mmol) and butyllithium (5 ml of a commercial solution in hexane, 7.65 mmol) in tetrahydrofuran (20 ml). This solution is added dropwise, over 40-60 min, to a stirred solution of palladium(II) chloride (0.06 g, 0.34 mmol), triphenylphosphine (0.18 g, 0.69 mmol), diisobutylaluminium hydride (0.5 ml of a commercial solution in toluene, 0.6 mmol), and iodobenzene (1.35 g, 6.65 mmol) in tetrahydrofuran (7 ml) under an argon atmosphere at room temperature. The lithium compound is kept at −70 °C during the addition period. Stirring is continued for 1 h at room temperature, the mixture then hydrolyzed with water (15 ml), extracted with pentane (3 x 100 ml), and the extract washed with saturated sodium chloride solution (5 x 10 ml). The volatile components are removed in vacuo and the residual product is rapidly chromatographed through a silica gel (20 g) column using pentane as eluent to give pure **4ba**; yield: 0.9 g (78%).

Phenyl Vinyl Ketone (7a):

Iodobenzene (2 g, 9.8 mmol) is added to a stirred solution in tetrahydrofuran (10 ml) of palladium(II) chloride (0.12 g, 0.68 mmol), triphenylphosphine (0.35 g, 1.36 mmol), and diisobutylaluminium hydride (0.84 mmol, 0.7 ml of a commercial solution in toluene), under an argon atmosphere. To the resultant mixture is added dropwise at 55 °C, over a 1 h period, a solution in tetrahydrofuran (30 ml) of 1-methoxy-1,2-propadienyllithium **(6a)** prepared just before use from methoxypropadiene (**5a**; 1 g, 14.29 mmol) and butyllithium (8 ml of a commercial solution in hexane, 12 mmol) at −30 °C under an argon atmosphere[9]. The lithium compound is kept at −30 °C during the addition period. The mixture is stirred for a further 30 min, allowed to reach room temperature, then hydrolyzed with 10% sulfuric acid (20 ml), extracted with pentane (3 x 100 ml), and the extract washed with saturated sodium chloride solution (5 x 10 ml). The volatile components are removed in vacuo, the residual product is filtered through a 5 cm silica gel column using pentane as solvent. The product is purified by bulb-to-bulb distillation; yield: 0.55 g (42%); b.p. 80 °C (bath)/0.1 torr.

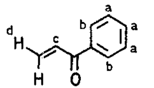
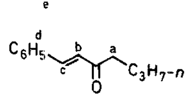
Table 1. Pd-Catalyzed Synthesis of Arylallenes **(4aa, 4ba)** and 1,2,4-Alkatrienes **(4ab, 4ac)**

Educts	Catalyst	Product	Yield[a] [%]	Molecular formula[b] or Lit. Data	I.R. (neat) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
1a+3a	$PdCl_2/2(C_6H_5)_3P/$ $AlH(i\text{-}C_4H_9)_2$	**4aa** 	90	b.p. 41-42 °C/ 0.25 torr[12]	1920 (C=C=C); 1580, 1485, 1450 (C_6H_5)	7.15 (m, 5H-a); 5.92 (m, H-b); 1.85 (d, $^5J_{allenic}$=3.5 Hz, 6H-c)
1b+3a	$PdCl_2/2(C_6H_5)_3P/$ $AlH(i\text{-}C_4H_9)_2$	**4ba** 	78	$C_{13}H_{16}$ (172.1)	1920 (C=C=C); 1580, 1480, 1450 (C_6H_5)	7.30 (m, 5H-a); 6.15 (dt, $^4J_{allenic}$ =6.5 Hz, $^5J_{allenic}$=3 Hz, H-b); 5.57 (dt, $^4J_{allenic}$=6.5 Hz, ^3J=6.5 Hz, H-c); 2.15 (m, 2H-d)
1a+3b	$Pd[P(C_6H_5)_3]_4$	**4ab** 	80	$C_{13}H_{22}$ (178.1)	1930 (C=C=C); 1625, 970 (C=C)	5.60 (m, H-b, H-c, H-d); 2.05 (m, 2H-a); 1.70 (d, $^5J_{allenic}$=2 Hz, 6H-e)
1a+3c	$PdCl_2/2(C_6H_5)_3P/$ $AlH(i\text{-}C_4H_9)_2$	**4ac** 	85	$C_{13}H_{22}$ (178.1)	1930 (C=C=C); 1625, 1420, 715 (C=C)	5.67 (m, H-b, H-c, H-d); 2.15 (m, 2H-a); 1.75 (d, $^5J_{allenic}$=2 Hz, 6H-e)

[a] Product isolated by chromatography on silica gel; yield based on **3** used.

[b] The mass spectra and the microanalyses were in satisfactory agreement with the calculated values: C, ±0.31; H, ±0.21.

Table 2. Pd-Catalyzed Synthesis of 1-Alkenyl Ketones **(7)**

Product	Yield[a] [%]	m.p. or b.p.[b]/torr [°C]		I.R. ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
		found	reported		
7a 	42	b.p. 78-80°/0.1	b.p. 115-117°/18[13]	(neat) 1660 (C=O); 1645 (C=C); 1600, 1570, 1485, 1445 (C_6H_5)	8.0 (m, 2H-b); 7.55 (m, 3H-a); 7.20 (dd, J_{trans}=18 Hz, J_{cis}=10 Hz, H-c); 6.45 (dd, J_{trans}=18 Hz, ^2J=2 Hz, H-e); 5.95 (dd, J_{cis}=10 Hz, ^2J=2 Hz, H-d)
7b 	78	38-39°	34-35°[14] 38-39°[15]	(in CCl_4) 1685 (C=O); 1660 (C=C); 1605, 1575, 1495, 1450 (C_6H_5)	7.60 (d, J_{trans}=16.5 Hz, H-b); 7.50 (m, 5H-d); 6.75 (d, J_{trans}=16.5 Hz, H-c); 2.65 (t, ^3J=7 Hz, 2H-a)

[a] Yield of isolated product based on C_6H_5J used.

[b] Oil bath temperature.

(*E*)-3-Oxo-1-phenyl-1-heptene (7b):
Iodobenzene (1.2 g, 5.9 mmol) is added to a stirred solution of palladium(II) chloride (0.08 g, 0.45 mmol), triphenylphosphine (0.24 g, 0.90 mmol), and diisobutylaluminium hydride (0.4 ml, 0.48 mmol) in tetrahydrofuran (5 ml) under an argon atmosphere. To the resultant mixture is added very slowly, dropwise at 55 °C over 1 h, a solution in tetrahydrofuran (25 ml) of 3-methoxy-1,2-heptadienyllithium[11] prepared just before use from 3-methoxy-1,2-heptadiene (**5b**; 1.15 g, 9 mmol) and butyllithium (5.5 ml of a commercial solution in hexane, 8.4 mmol) at −30 °C under an argon atmosphere. The lithium compound is kept at −30 °C during the addition period. Stirring is continued for 30 min, the mixture then allowed to reach room temperature, hydrolyzed with 10% sulfuric acid (15 ml), and extracted with pentane (2 x 100 ml). The extract is washed with saturated sodium chloride solution (5 x 5 ml), the volatile components are removed, and the residue is filtered through a 5 cm silica gel column using pentane as solvent. The product is recrystallized from pentane at −40 °C as yellow needles; yield: 0.86 g (78%); m.p. 38 °C.

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