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The Stille coupling reaction of aryl triflates with n-tributylallenyl stannane : a general route to arylallenes.

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Abstract: The palladium-copper co-catalyzed cross-coupling reaction of n-tributylallenyl stannane 1 with aryl triflates provides an efficient route to the corresponding aryl allenes.

The unique structure and reactivity of allenes have prompted many investigations of synthesis with these compounds.(1) In spite of this broad interest, few methods for the synthesis of simple Ar-CH=C=CH_2 have been developed. The acid-catalyzed dienone-phenol (2) rearrangement and the Lewis acid-catalyzed propargylphenylethers rearrangement(3) are elegant, good-yield reactions, but unfortunately they provide only o-o'-disubstituted-3-allenylphenols. Ruitenberg et al.(4) and Graaf et al.(5) have shown that allenyl zinc or magnesium compounds react with aryl iodides to yield the corresponding aryl allenes. With many reactive functional groups, e.g., esters and ketones, this method requires protection/deprotection steps to avoid reaction at the sensitive group.

The palladium coupling of organotin reagents with aryl halides or triflates,(6) now referred to as the Stille reaction, is compatible with virtually any functional group, eliminating the need for protection strategies.

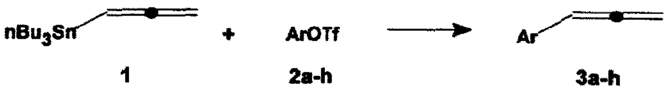
A recent paper describes the Stille coupling of stannyl allenes with unsubstituted aromatic iodides.(7) Notably, the authors report failure to achieve this coupling with aryl triflates under the conditions employed.

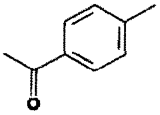
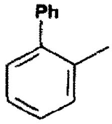
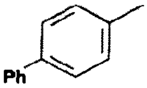
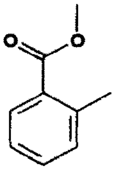
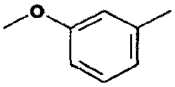
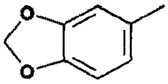
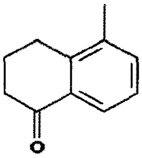
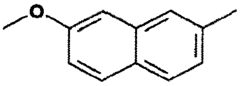
In this communication, we wish to report the application of the Stille reaction to the synthesis of aryl allenes 3 from the corresponding aryl triflates 2 and allenyltributyltin 1.(8)(Scheme)

SCHEME

Explorative studies of the coupling of 1 with *p*-acetylphenyl triflate 2a under various

TABLE. Palladium-catalyzed coupling of 1 with various aryltriflates.(a)



entry	Ar-	t(h)	Product	Isolated yield %
1		1	**3a**	60
2		5	**3b**	20[b]
3		5	**3c**	31[b]
4		1.5	**3d**	71
5		2	**3e**	70
6		2	**3f**	24[b]
7		1.5	**3g**	60
8		1.5	**3h**	67

a) reactions were carried out at 80°C. b) Reaction did not go to completion.

reaction conditions were done. Under Farina's conditions (9) [LiCl, $Pd_2(dba)_3$, tris(2-furyl)phosphine (TFP), DMF or N-methylpyrrolidone (NMP)] at 80°C we were unable to obtain yields of **3a** greater than 28%. The observation that copper(I) iodide co-catalyses the Stille reaction of aryl- and vinyl- iodides or bromides(10) prompted us to carry out the coupling in the presence of CuI.

Using 2% $Pd_2(dba)_3$, 8% TFP, 3 equiv.LiCl and 10% purified CuI (11) in DMF (NMP was less effective) at 80°C we obtained **3a** in 60% yield. In addition the reaction took 1h to reach completion, while in the presence of the palladium catalyst alone, the reaction was considerably slower (3-4h).

It should be noted that triphenylarsine-based palladium catalyst provided a complex reaction mixture in which there was no **3a**. This was rather surprising, because catalysts including triphenylarsine usually give the fastest rates of Stille cross-coupling reactions. (9,10b-c)

To generalize the use of the tributyl allenylstannane-aryl triflate coupling protocol, **1** was treated with a variety of aryl triflates.(12) (Table)

These results show that this coupling reaction is applicable to aryl triflates with various substituted functional groups. The yields obtained were good, except for aryl triflates with electron-donating groups, which reacted only partially (entries 2,3 and 6).

In a typical procedure (entry 4), 2-(triflyloxy)methylbenzoate **2d** (580 mg,2.04 mmol) was dissolved in DMF (5.1 mL) and treated with anhydrous LiCl (258 mg,3 equiv), TFP (38 mg, 0.08 equiv), $Pd_2(dba)_3$ (37.3 mg,0.04 equiv of Pd) and CuI (39 mg, 0.1 equiv). After 5 min at room temperature, **1** (739 mg, 2.24 mmol) was added and the suspension was stirred under argon at 80°C for 1.5 h. Dilution with saturated KF solution and ether, filtration and separation of the organic phase were followed by drying and evaporation. Silica gel flash chromatography (13) (15% ethyl acetate in petroleum ether) gave **3d** (colorless oil, 250 mg, 71%): IR (neat) 2950, 1938, 1718 cm $^{-1}$; ^{1}HNMR ($CDCl_3$) δ 7.89 (m,1H), 7.6 (d,J=7.9 Hz,1H), 7.45 (m,1H), 7.22 (m,2H), 5.12 (d,J=6.8 Hz,2H), 3.9 (s,3H).

At present, we are exploring the possibility to extend the allenylstannane-aryltriflate coupling to the synthesis of Ar-CH=C=CH-R.

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