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Synthesis of Allyl Aryl Sulphides by Palladium(0)-mediated Alkylation of Thiols

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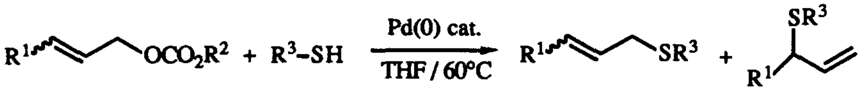
Key Words: allylic carbonates; allylic alkyl sulphides; palladium-catalyzed *S*-alkylation

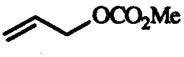
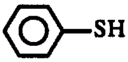
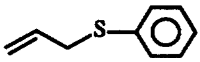
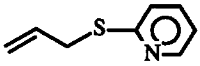
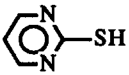
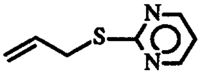
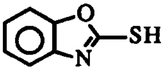
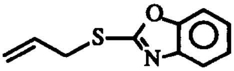
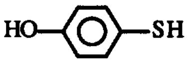
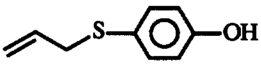
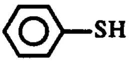
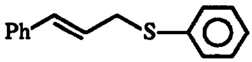
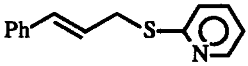
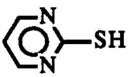
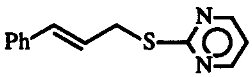
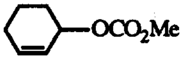
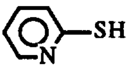
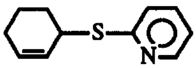
Abstract: Various allylic aryl sulphides are readily prepared in high yields by the palladium(0)-catalyzed *S*-alkylation of allylic carbonates by various aromatic thiols.

Palladium(0)-catalyzed nucleophilic substitution of allylic compounds having an increasing number of applications in synthetic strategies, mainly due to the facile reaction of the allylic substrates and the high stereospecificity of the reaction.[1] However, although catalytic allylation is usually carried out with carbon, nitrogen and oxygen nucleophiles, there are only two reports on the C-S bond formation using this methodology.[2] Under classical allylation conditions, sulfur nucleophiles either precipitate the catalyst from solution or tie-up the palladium complex in an unreactive form. An elegant solution avoiding the precipitation or complexation of the catalyst was the use of an *O*-allyl *S*-alkyl dithiocarbonate[2a] or of silylated thiol[2b] allowing the quantitative formation of an allyl alkyl sulphide. However the major drawback of these methodologies is the preparation, for each sulfur nucleophile, of the corresponding *O*-allyl *S*-alkyl dithiocarbonate or silylated thiol. We have recently described the alkylation of allylic carbonates with oxygen nucleophiles.[3] In this communication, we present preliminary results (Table 1) showing that this methodology could be advantageously used with sulfur nucleophiles according to Scheme 1.



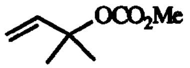
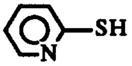
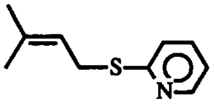
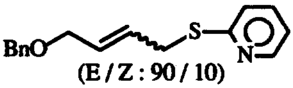
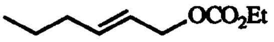
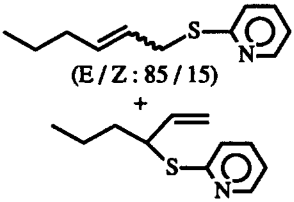
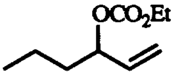
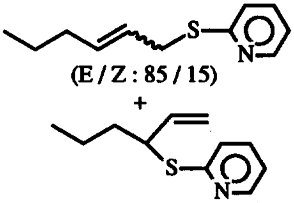
Scheme 1

Table 1. Pd(0)-Mediated Allylation of Thiols using Allylic Carbonates.[a]

Entry	Carbonate	Thiol	Product(s)[b]	Yield(%)[c] (ratio)[d]
1				83
2	"			86
3	"			77
4	"			44
5	"			87
6				60
7	"			74
8	"			76
9				89

(continued)

Table (continued)

Entry	Carbonate	Thiol	Product(s)[b]	Yield(%)[c] (ratio)[d]
10				51
11			 (E / Z : 90 / 10)	92
12			 (E / Z : 85 / 15) +	98 (95/5)
13			 (E / Z : 85 / 15) +	96 (98/2)

[a] All reactions were run under nitrogen in tetrahydrofuran at 60°C during 12 h. [carbonate]: [thiol]: [Pd]: [phosphine] = 30: 25: 1: 2. [b] All products gave the expected ^1H,^{13}C NMR, IR and combustion analysis data (C, H). [c] Isolated yields and not optimized. [d] Determined by ^1H and ^{13}C NMR.

The results summarized in Table 1 indicated that the *S*-alkylation reaction works well with a variety of carbonates containing 1°, 2° and 3° allylic groups and thiols, giving generally quite high yields. It is noticeable that 2-mercaptobenzoxazole (entry 4) and thiophenol (entry 5) only gave the allyl alkyl sulphide. In the case of ethyl cinnamyl carbonate (entries 6-8) we only observed the formation of the *E*-cinnamyl aryl thioether, in agreement with the results found using phenol as the nucleophile.[3d]

Allylic rearrangements consistent with a π-allyl palladium intermediate are observed (entries 10, 12 and 13). Regioisomeric allylic carbonates (entries 12 and 13) gave identical mixtures of regio and stereoisomeric sulphides, the more highly substituted alkene being predominant (95%), but as a mixture 85/15 of *E* and *Z* isomers ; this behaviour is different from the reaction with phenol, where only the *E* isomer was observed.[3d] A single isomeric product was observed when the allylic termini were substantially sterically different (entry 10). We noticed also that a *Z*-allylic carbonate (entry 11) gave a mixture (90/10) of *E* and *Z* allylic sulphides.

Mechanistically, this process proceeds via a π-allyl palladium species; exchange of the alkoxide with the thiol gives the nucleophile and *S*-alkylation reaction takes place in a similar manner to the mechanism previously described in the *O*-alkylation reaction.[3a] The success of this *S*-alkylation is due to the fact that the nucleophile is produced during the catalytic cycle, so in concentrations wich are never higher than those of the π-allyl palladium intermediate.

In conclusion, this process provides a very valuable route to allylic alkyl sulphides starting from easily accessible carbonates.

General Procedure: A mixture of dipalladium tris(dibenzylideneacetone) (27.5 mg, 0.03 mmol), 1,4-bis(diphenylphosphino)butane (51.2 mg, 0.12 mmol), carbonate and thiol in THF (5ml) was stirred under a nitrogen atmosphere at 60°C for 12 h. Concentration in vacuo and chromatographic purification (SiO_2) of the residue provided the adduct(s).

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