Homogeneous Catalysis. Production of Allyl Alkyl Sulphides by Palladium Mediated Allylation

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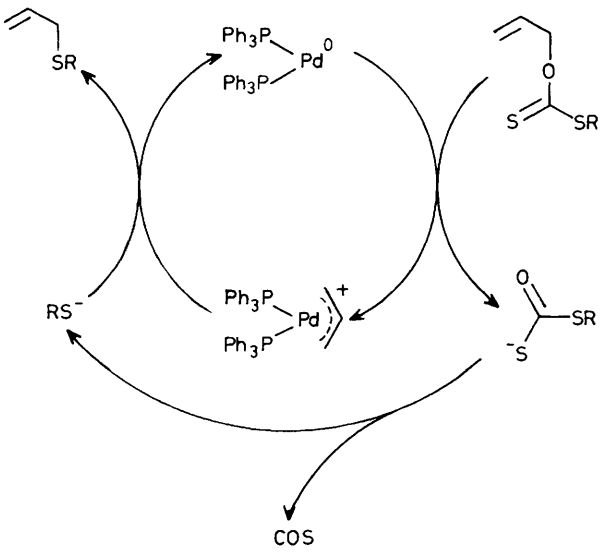
The use of *O*-allyl *S*-alkyl dithiocarbonate substrates in palladium mediated catalytic allylation gives carbonyl sulphide and allyl alkyl sulphides with net retention of configuration and their use obviates the problems associated with sulphur nucleophiles in catalytic allylation.

Catalytic allylation using phosphine–palladium complexes and allylic acetates has been carried out with oxygen, nitrogen, and soft carbon nucleophiles[1,2] but not with sulphur nucleophiles. The usual allylation conditions involve the use of 5 mol. % of a palladium(0)–phosphine complex and equimolar amounts of the allylic acetate and the nucleophile. Under these circumstances sulphur nucleophiles either precipitate the catalyst from solution or tie-up the palladium in a form that is unreactive when the catalyst remains in solution. Since catalytic allylation is finding increasing application in synthetic strategies,[1–4] we entertained various approaches to circumventing the problem associated with sulphur nucleophile allylation. Aside from finding ways of avoiding the precipitation or complexation of the catalyst, we also sought a system for which the substrates were easy to prepare and for which the catalytic turnover was quick and devoid of side products. We present here one solution which meets these criteria. The idea is illustrated in Scheme 1.

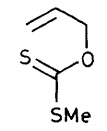
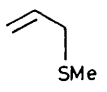
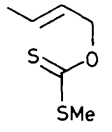
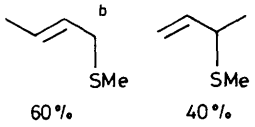
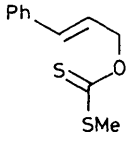
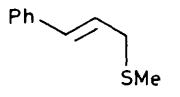
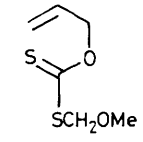
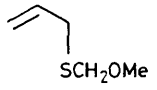
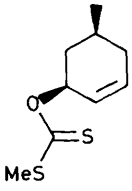
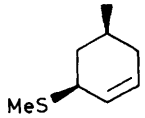
The *O*-allyl *S*-alkyl dithiocarbonate oxidatively adds to the palladium(0)-phosphine complex to produce the π-allyl palladium(II) intermediate together with the *S*-alkyl dithiocarbonate ion. The latter, an unstable species, spontaneously releases COS and the RS^- nucleophile which then attacks the π-allyl intermediate to give the allyl alkyl sulphide and completes the catalytic cycle.

The advantage of this scheme is that the nucleophile is produced on demand in concentrations which are never higher than those of the π-allyl intermediate. Although it is conveivable that either COS or RS^- could interfere with the catalytic activity by co-ordination, particularly to the palladium(0) species, we have encountered no such catalytic poisoning. It should be noted, however, that the *O*-allyl *S*-alkyl dithiocarbonates undergo relatively facile Claisen rearrangements[5] which may compete if the allylation is slow. This does not appear to be a problem because allylation is generally much faster.



Scheme 1

Table 1. Catalytic allylation using *O*-allyl *S*-alkyl dithiocarbonates in chloroform solution with $[Pd(PPh_3)_4]$ at 25 °C.

Entry	Substrate	Reaction time	Product (+COS)
i		20 min	
ii		3 h	 60% 40%
iii		30 min	
iv		3 h	
v		1 h	

[a] Approximate time for >95% allylation. [b] High field ^1H n.m.r. showed approximately 20% of the *cis*-olefin isomer.

The allyl substrates are easy to prepare;[5] the potassium salt of the allyl alcohol was treated with CS_2 and the resulting dithiocarbonate ion was alkylated. The allylation was carried out by simply mixing the *O*-allyl *S*-alkyl dithiocarbonate substrate with 5 mol. % of $[Pd(PPh_3)_4]$ in a suitable solvent. The progress of reaction was followed by n.m.r. spectroscopy.

Table 1 contains a representative collection of results. All the reactions were devoid of side products and COS was detected by i.r. spectroscopy in the catalytic solutions. The first three entries serve to illustrate the method. As is generally found for 1- or 3-substituted alkyl substituted allyls (entry ii) allylation is not regioselective, and a mixture of products is obtained. For the corresponding substrates with π-conjugating groups (entry iii), allylation generally gives the product with the double bond in conjugation.[3] Thus the sulphur nucleophiles behave in a manner similar to that observed for other nucleophiles.

In addition to the catalytic production of allyl alkyl sulphides, we sought a modification which would give allyl thiols. Entry iv provides such an example where the substrate is a derivative of chloromethyl methyl ether. The catalytically released nucleophile, $MeOCH_2S^-$, is a protected sulphydryl anion equivalent which upon allylation gives the corresponding sulphide. This allyl sulphide is readily converted into the allyl thiol by a number of mild deprotecting agents.[6]

The last entry (v) illustrates the stereochemistry of the sulphur allylation, the reaction proceeding with overall retention of geometry. The stereochemistry of the product was established by (Claisen) rearrangement of the potassium salt of the *O*-allyl dithiocarbonate[7,8] followed by methylation of the produced mercapto anion. It has been established that oxidative addition to palladium(0) complexes by a variety of allylic substrates proceeds with inversion of configuration.[4,9-11] Assuming this to be the case here, then it follows that the nucleophilic attack step (Scheme 1) also proceeds with inversion. This conclusion implies that the sulphur nucleophile undergoes conventional addition to the π-allyl intermediate; namely, it attacks the *exo*-face of the co-ordinated π-allyl and there appears to be no contribution from a path involving prior co-ordination of the nucleophile followed by *endo*-face reductive elimination.

A thermal uncatalysed analogue of the present reaction was reported recently.[12] Thus thermolysis of *O*-allyl *S*-alkyl dithiocarbonates leads to the *S*-alkyl allyl sulphides and COS by two sequential [3,3] sigmatropic rearrangements. Using the reported kinetic data, we calculate that our catalytic system provides a rate acceleration of about 10^5 over the thermal uncatalysed path.

Finally, we should point out that Tsuji[13] has employed allyl carbonates in a similar manner for palladium catalysed allylation using convential nucleophiles.

The present results expand the versatility of palladium mediated catalytic allylation and provide one solution to the problems associated with the use of sulphur nucleophiles for allylation.

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