Steric Effect of Substituents in Allylic Groups in Oxidative Addition of Allylic Phenyl Sulphides to a Palladium(0) Complex. C–S Bond Cleavage triggered by Attack of Pd on the Terminal Carbon of the C=C Double Bond

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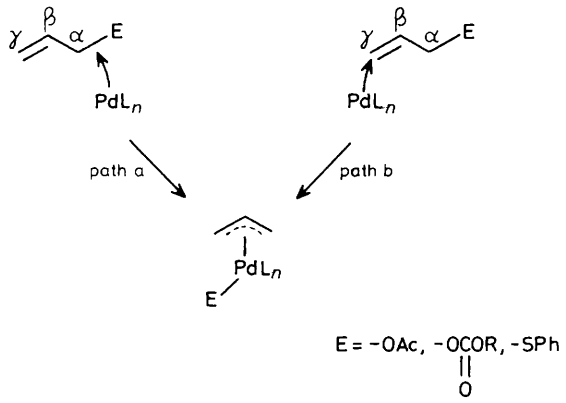
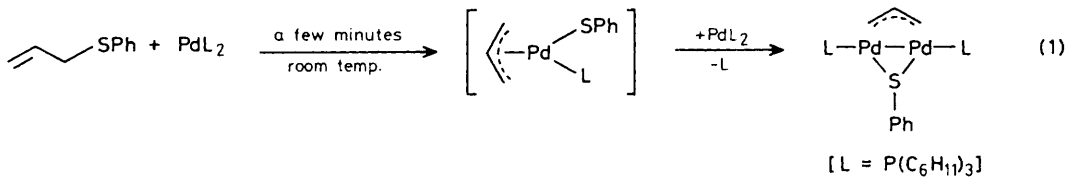
In the oxidative addition of allylic phenyl sulphides to $Pd[P(C_6H_{11})_3]_2$ a methyl or phenyl substituent at C(γ) of the allylic system C(γ)=C(β)–C(α)–SPh retarded the reaction to a much greater extent than a substitu nt at C(α), indicating that the oxidative addition involving C(α)–S bond cleavage involved attack of Pd on C(γ) as a crucial step.

Palladium-catalysed allylation using allylic acetate,[1] allylic carbonate,[2] and allylic sulphide[3] as the allylating reagents has found extensive application in synthetic organic reactions.



Scheme 1

Recent studies of these reactions clarified the stereochemistry of the reaction, which is explained by assuming (a) formation of an intermediary π-allyl palladium complex by C(α)–O or C(α)–S bond cleavage in C(γ)=C(β)–C(α)–E (E = OR, SR) and (b) subsequent external attack of a nucleophile on the π-allyl ligand, both processes proceeding with stereochemical inversion at C(α).[4] However, it has not been revealed whether the oxidative addition of the C–O or C–S bond to Pd(0) proceeds by direct insertion of the metal centre to the C–O or C–S bond (path a in Scheme 1) or by attack of Pd(0) on C(γ) which induces elimination of the leaving group (path b). Previously we reported that a reaction of allyl phenyl sulphide with $Pd[P(C_6H_{11})_3]_2$ gave $[(C_6H_{11})_3P]_2Pd_2(\mu\text{-}C_3H_5)(\mu\text{-SPh})$.[5] This reaction is considered to proceed through C–S bond cleavage of the sulphide to give $Pd(\pi\text{-}C_3H_5)(SPh)[P(C_6H_{11})_3]$ followed by its coupling with another $Pd[P(C_6H_{11})_3]_2$ (equation 1). When the non-substituted allyl phenyl sulphide is used, the above reaction is completed within a few minutes at room temperature. In this paper we report a remarkable dependence of the reactivity of allylic phenyl sulphides on the

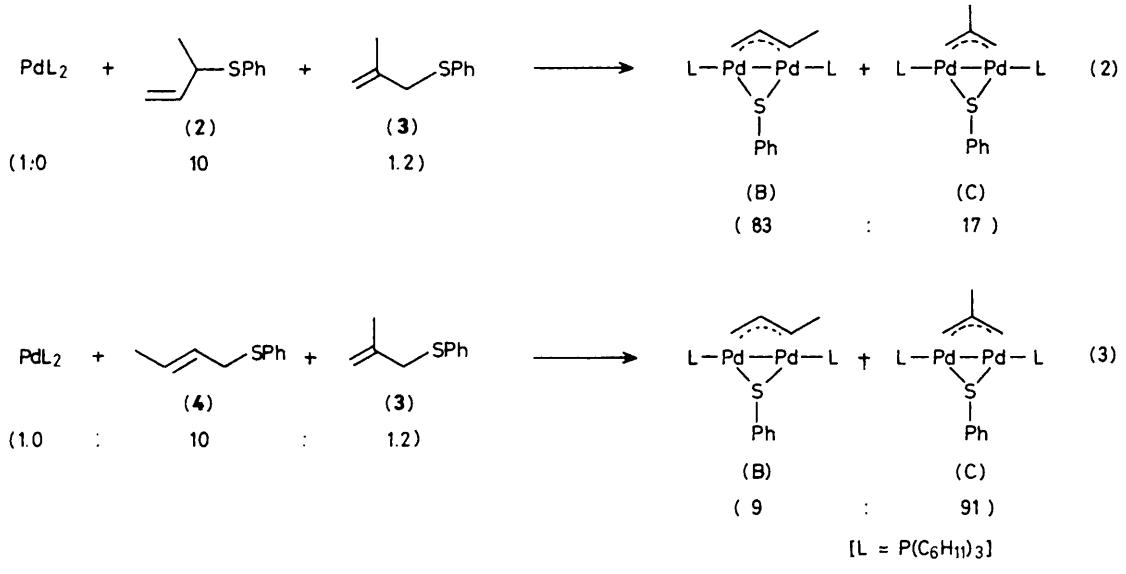


(1)

Table 1. Reactions of allylic phenyl sulphides with $Pd[P(C_6H_{11})_3]_2$ (see Scheme 2).[a]

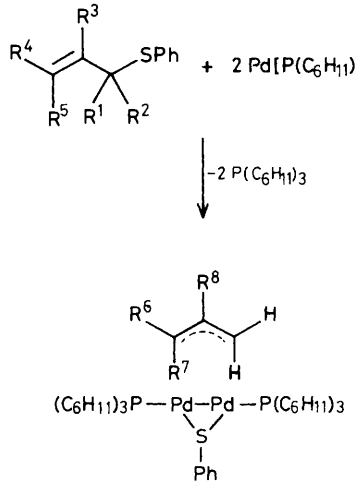
	Substituent[b] in sulphide	$Pd[P(C_6H_{11})_3]_2$: Sulphide	Reaction[c] time		Product yield (%)	
(1)	$R^1 = R^2 = Me$	1:1	<20 min	(A)	$R^6 = R^7 = Me$, $R^8 = H$	(85%)
(2)	$R^1 = Me$	1:1	<10 min	(B)	R^7 (or R^6) = Me, R^6 (or R^7) = R^8 = H[d]	(73%)
(3)	$R^3 = Me$	1:1	<10 min	(C)	$R^8 = Me$, $R^6 = R^7 = H$	(90%)
(4)[e]	R^4 (or R^5) = Me	1:3	>7 h	(B)	R^7 (or R^6) = Me, R^6 (or R^7) = R^8 = H[f]	(61%)
(5)	$R^4 = Ph$	1:3	>7 h	(D)	$R^6 = Ph$, $R^7 = R^8 = H$	(91%)
(6)	$R^4 = R^5 = Me$	1:1			No reaction	

[a] In benzene solution at room temperature. [b] Other R^1—R^5 = H. [c] Time required for completion of the reaction as observed by $^{31}P\{^1H\}$ n.m.r. [d] *syn* (R^6 = Me) : *anti* (R^7 = Me) = 40:60. Prolonged reaction caused complete conversion of the mixture into the *anti* isomer. [e] (*E*) : (*Z*) = 78:22. [f] *syn* : *anti* = 68:32.



steric environment of the allylic system, supporting the mechanism through path b.

Use of various allylic phenyl sulphides (**1**), (**2**), (**3**), (**4**), and (**5**) shown in Table 1 in the reaction with $Pd[P(C_6H_{11})_3]_2$ gave the corresponding dinuclear μ-allyl complexes (A), (B), (C), (B), and (D), respectively. All these complexes were characterized by n.m.r. (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra as well as by elemental analysis. The sulphides, C(γ)=C(β)–C(α)–SPh, having one or two methyl groups on C(α) or C(β), (**1**), (**2**), and (**3**), readily underwent C–S bond cleavage and the formation of the corresponding dinuclear μ-allyl complexes was completed within 20 minutes at room temperature. On the other hand, sulphides having γ-substituents, (**4**) and (**5**), required more than 7 h for the completion of the reaction as followed by $^{31}P\{^1H\}$ n.m.r. spectroscopy. Compound (**6**) with two methyl substituents on the γ-carbon did not undergo oxidative addition at room temperature even after 2 days, while the anticipated reaction product (A) (see the first run in Table 1) was easily obtained from the reaction of α-disubstituted sulphide (**1**) with $Pd[P(C_6H_{11})_3]_2$.



Scheme 2

Competitive reactions using (**2**), (**3**), and (**4**) were carried out to obtain the results shown in equations (2) and (3). The results clearly indicate that (**2**) and (**3**) have comparable reactivity towards the Pd(0) complex whereas (**4**), giving the same product as (**2**), has much lower reactivity than (**3**).

All these results indicate that the substitution at C(α), near the cleaved bond, affects the reactivity towards the oxidative addition to a minor extent, whereas substitution at the farther position, C(γ), lowers the reactivity of the reactant greatly. The steric effects of the reactants are accounted for more reasonably by assuming the S_N2'-type reaction mechanism[6] (path b) involving attack of palladium at C(γ) followed by expulsion of the PhS group from the *exo* position of the allylic sulphide. This type of clear steric effect of allylic compounds on the oxidative addition to transition metal complexes has no precedent.

A recent paper on palladium catalysed reaction of *O*-allyl *S*-alkyl dithiocarbonate to give allyl alkyl sulphide and COS showed that the reaction was retarded by the presence of a γ-substituent on the substrate.[7] This is probably due to the hindrance of the substituent in oxidative addition of the substrate to Pd(0) species giving a π-allyl intermediate.

Received, 23rd June 1986; Com. 861

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