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THE γ-FUNCTIONALISATION OF α,β-UNSATURATED KETONES VIA π-ALLYLPALLADIUM COMPOUNDS

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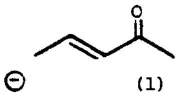
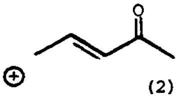
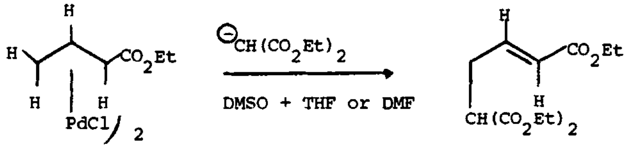
There has been much recent interest in synthetic transformations which invert the inherent chemical reactivity that functional groups confer on an organic molecule.[1] Thus the γ-carbon atom of an α,β-unsaturated carbonyl system is normally a potential enolate (1) but when converted into a π-allylpalladium complex we now demonstrate that the γ-carbon atom behaves as an electrophilic synthon (2).

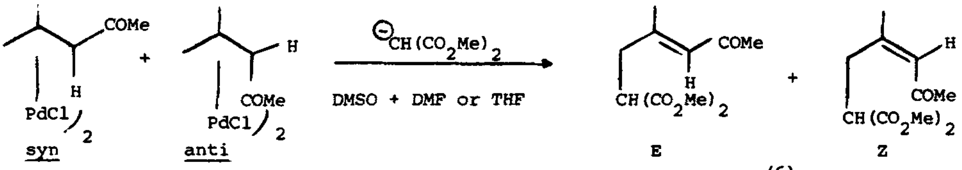

(1)


(2)

In this manner di-μ-chloro-bis-[1,2,3-trihapto-(1-ethoxycarbonylallyl)palladium (II)] (3) reacts with diethylmalonate to give the substitution product (4) when dimethylsulphoxide (DMSO) is used as cosolvent in approximately equal volume with either tetrahydrofuran, ethan or dimethylformamide (DMF). The reaction proceeds in quantitative yield and is both regio- and stereospecific. Reaction is entirely at the carbon atom γ to the carboxylate group and the syn-stereochemistry of the allylpalladium complex[2] is retained in the E-stereochemistry of the product (4). Mesityl oxide gave a mixture of syn- and anti-palladium complexes (5)[3] which reacted with malonate ion under the above conditions to give the E- and Z-isomers of (6) in 90% yield. The conversion was not stereospecific in that the ratio of stereoisomers varied with conditions but the E-isomer was always the major isomer in the product whereas

(3)


(4)



(5)

(6)

the *anti*-isomer was in slight excess in the π-allyl compound.[+]

The publications of Trost and his co-workers[4] suggest that the presence of an additional ligand facilitates substitution in the allyl system. The dimethylsulphoxide probably fulfils this role as well as acting as a convenient co-solvent both in our work and that reported previously for reactions with simple π-allyl compounds.[5] In agreement with Trost's proposals no reaction occurred in the absence of DMSO in either THF or DMF but addition of triphenylphosphine (4 mol. equiv.) to a reaction of (3) with malonate in THF gave (4) in 70% yield. Reactions of (3) and (5) with other soft nucleophiles, e.g. the anions from ethyl cyanoacetate and ethyl methylsulphonylacetate, also gave high yields of substitution products but no reaction occurred with the harder nucleophile, cyanide ion, under similar conditions. The yields for a series of reactions between π-allyl complex (0.5 mmole) and nucleophile (1.2 mmole) for 5 - 7 h at ambient temperature in DMSO (5 cm^3) and the designated solvent (5 cm^3) are tabulated below -

	Yields (%) for reactions of nucleophiles		
π-Allyl complex	Diethyl malonate	Ethyl methylsulphonyl acetate	Ethyl cyanoacetate
3	90 EtOH	72 EtOH, 58 DMF	79 EtOH
5	100 EtOH	80 EtOH, 75 DMF	60 EtOH

We thank Johnson and Matthey Ltd. for a loan of palladium and Professor Barry M. Tros for comment.

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[+] Stereochemical assignments were based on the downfield shift of a methyl group *cis* to an acetyl function: L. M. Jackman and R. H. Wiley, J. Chem. Soc., 1960, 2881. The *reaction* may still be stereospecific as the *syn*- and *anti*-isomers of π-allylpalladium compounds are known to equilibrate under conditions similar to those used.