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Short Research Article

# Some investigations of the exchange-labelling of allyl terminal methylene groups over palladium catalysts†

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## Introduction

The isotopic exchange labelling of the terminal methylene groups of allyl and related systems with deuterium and tritium has been documented previously.[1] Often such labelling is merely a transitional step during the complete reduction of these systems. In such cases the resulting labelled hydrocarbon moiety bears an excess (sometimes very large) of isotope in the terminal methyl group.[2] As part of a more general series of investigations of the exchange processes accompanying alkene hydrogenations[3] we have recently investigated this terminal exchange process in some detail using $D_2$, or DT with the allyl systems below (Figure 1).

## Results and discussion

All the substrates readily underwent the isotopic exchange process. In addition, for those substrates in which the appropriate resonances could be resolved by $^1$H- and $^2$H-NMR, analysis, the exchanged product showed an approximately equal amount of deuterium in both of the terminal *cis* and *trans* positions (Figure 2). It could be that both the terminal positions have achieved a similar equilibrium despite the limited isotopic hydrogen pool and the subsequent consecutive

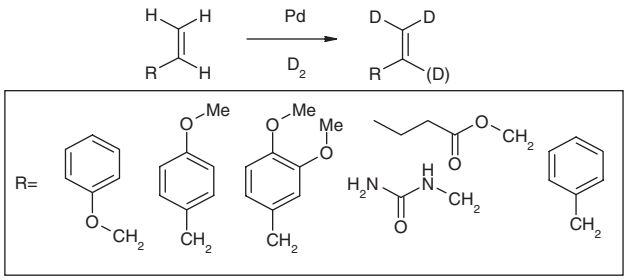


**Figure 1** Model allyl systems.

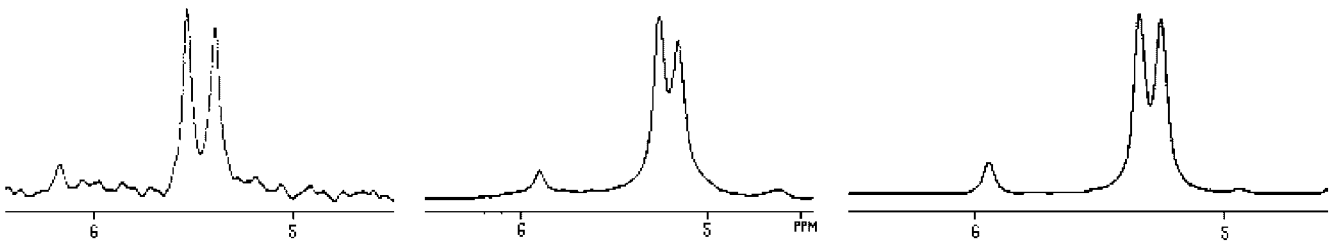


**Figure 2** $^2$H-NMRs of partially deuterogenated alkenes in the olefinic region. Left to right: allyl phenyl ether, allylurea, allyl butyrate.

hydrogenation reaction. Alternatively their exchange rates could be very similar, although this seems unlikely given the disparate chemical structures. More likely is a loss of stereochemical integrity via the formation of one or more symmetrical intermediates during the reaction. This seems probable if, as

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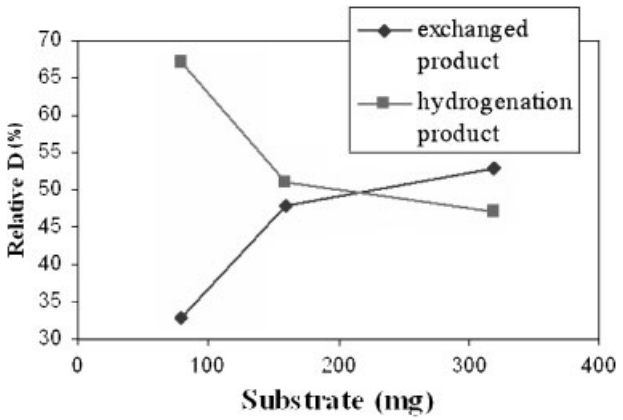


**Figure 3** Exchange vs reduction for allyl butyrate in THF (1 ml) using $D_2$ (0.4 mmol) over 5% palladium on carbon (10 mg) for 18 h.

expected, primary or secondary Pd alkyls are involved in the exchange.

Moreover, the results presented (Figure 3) also suggest that the exchange of terminal methylene groups in allyl systems, using a deficit of isotopic hydrogen, could provide a viable route to the terminal hydrogen isotope labelling of such systems, provided the appropriate separation systems are available.

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