Hydroformylation of [1-^{14}C]Propene

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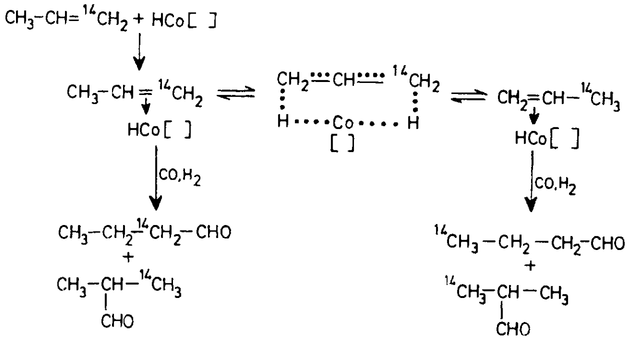
Summary The hydroformylation of [1-^{14}C]propene under high CO and H_2 pressure in the presence of $Co_2(CO)_8$ gave [2-^{14}C]-n-butanal (48%), [4-^{14}C]-n-butanal (32%), and 2-methyl[3-^{14}C]propanal (20%).

The cobalt-catalysed hydroformylation of olefins under a relatively high pressure of carbon monoxide is, according to previous work on optically active and various substituted olefins,[1,2] neither accompanied by nor preceded by olefin isomerization. The formation of products due to the insertion of a formyl group at carbon atoms of the olefinic chain which are not part of the double bond of the initial olefin has been suggested as taking place through a rearrangement of an olefin–catalyst intermediate.[2]

In order to gain more information on the behaviour of this intermediate we have studied the hydroformylation of [1-^{14}C]propene. A shift in the position of the double bond in propene leads to an identical olefin, and so the position of the double bond is not influenced by steric or electronic effects. By using [1-^{14}C]propene, the proportion by which the formyl group of the n-butanal formed arises from addition to either of the terminal atoms may be determined from the position and extent of labelling in the reaction product.

[1-^{14}C]Propene, synthesized and analysed as described by Calvin,[3] was hydroformylated at 100 °C in the presence of CO and H_2 (1 : 1, 200 atm) and $Co_2(CO)_8$. The ratio of n-butanal to 2-methylpropanal in the products was 80 : 20 as expected. The aldehydes produced were separated and the ratio of [2-^{14}C]-n-butanal to [4-^{14}C]-n-butanal was determined by converting the n-butanals into propene and then analysing the propene by Calvin's procedure.[3]

The ratio of [2-^{14}C]-n-butanal to [4-^{14}C]-n-butanal was 60 : 40, indicating that the olefin–catalyst intermediate is not of an allylic type since, if this were the case, with propene as substrate we should have obtained equal insertion of the formyl group at the two ends of the olefinic chain.



Scheme

The formation of aldehyde products arising from formylation of either of the terminal atoms of propene cannot be explained by an isomerization *via* σ-bonded alkylcobalt carbonyls[4] and therefore it must be interpreted in terms of a rearrangement of an olefin–catalyst intermediate preceding the formation of alkylcobalt carbonyls. Complexes of this type, although never isolated, appear as the most likely precursors of alkylcobalt carbonyls. Isomerization of these complexes through hydrogen transfer along with a shift of the double bond in the organic unit would give rise to the various products (see Scheme).

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