Transition Metal-catalysed Rearrangement of Allyl But-3-enoate to Hepta-2,6-dienoic or Hepta-3,6-dienoic Acids

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Summary The rearrangement of allyl but-3-enoate to heptadienoic acids is catalysed by nickel and rhodium complexes in the presence of phosphorus-containing ligands and can be driven towards either the 2,6- or the 3,6-isomers through selective hydrogen abstraction.

SEVERAL catalytic insertion reactions of olefins and carbon monoxide into allyl–nickel bonds have been described by us previously.[1] We now report a new catalytic insertion reaction not involving carbon monoxide and leading to the rearrangement of allylic esters of but-3-enoic acid to 2,6- or 3,6-heptadienoic acids [equation (1)].

$$\mathrm{CH_2{=}CHCH_2CO_2CH_2CH{=}CH_2} \longrightarrow \left\{\begin{array}{c}\mathrm{CH_2{=}CHCH_2CH_2CH{=}CHCO_2H}\\ \mathbf{(1)}\\ \mathrm{CH_2{=}CHCH_2CH{=}CHCH_2CO_2H}\\ \mathbf{(2)}\end{array}\right. \qquad (1)$$

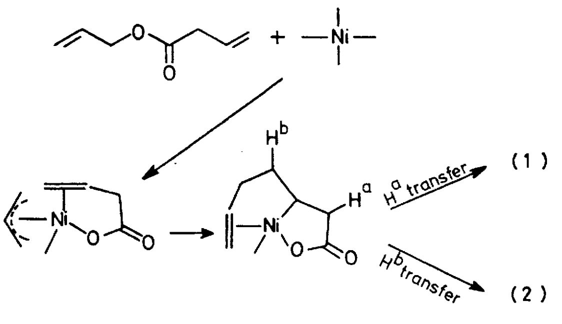
This rearrangement easily occurs at room temperature using nickel(0) complexes with phosphines or phosphites. It is highly selective (for allyl esters of but-3-enoic acid and not for those of but-2-enoic or pent-4-enoic acids) and regioselective (only the C atom of the double bond of the but-3-enoic acid takes part in the reaction). With nickel complexes in certain solvents such as anisole at room temperature the reaction is also stereoselective, the main product being the *trans*-2,6-isomer.

Thus bis(cyclo-1,5-octadiene)nickel [$Ni(cod)_2$] (10·5 mmol), tri-isopropyl phosphite (10·5 mmol), and allyl but-3-enoate (260 mmol), in anisole (130 ml) at 20 °C for 6 days under nitrogen gave *trans* (**1**) (140 mmol), (**2**) (*cis,trans*) (15 mmol), and the corresponding allyl esters (16·5 mmol; combined yield as free acids 66%). *trans*-4-Allylhepta-2,6-dienoic acid (20 mmol) was also formed.

With $Ni[P(OPr^i)_3]_4$ (0·9 mmol) and allyl but-3-enoate (180 mmol) in tetrahydrofuran (THF) at 80 °C for 15 h, the free acids (**1**) and (**2**) (94 mmol; ratio 1 : 2) and their allyl esters were formed (37 mmol; combined yield as free acids 73%).

The use of different phosphorus-containing ligands also influences the 2,6 : 3,6 ratio. The data available so far suggest that the ability to dissociate plays a major role in determining this ratio, bulky phosphines and phosphites giving the highest value [from 14 : 1 with tri-*o*-tolyl phosphite to 0·8 : 1 with triethyl phosphite in THF at 80 °C for 3 h, substrate : ligand : $Ni(cod)_2$ molar ratio 8 : 1 : 1]. The same trend was observed on passing from 1 to 4 mol of ligand per mol of complex. Excess of allyl but-3-enoate has a similar influence because the substrate also acts as ligand.

The 3,6-isomer is the less stable thermodynamically. It is not formed by isomerisation of the 2,6-isomer under the same reaction conditions. Different nickel-bonded intermediates, favouring proton abstraction from one of the two carbon atoms adjacent to the nickel–carbon bond formed by insertion, should therefore be assumed, as shown in the Scheme.



SCHEME

The Scheme is further substantiated by the presence of 4-allylhepta-2,6-dienoic acid as by-product, resulting from the same type of rearrangement undergone by allyl but-3-enoate [equation (2)].

$$CH_2{=}CHCH_2CH{=}CHCH_2CO_2CH_2CH{=}CH_2 \longrightarrow (CH_2{=}CHCH_2)_2CHCH{=}CHCO_2H \qquad (2)$$

Even in this case regioselectivity of the attack at the 3-double bond of the hepta-3,6-dienoic acid is retained, only the 4-C atom being affected.

Higher allyl esters are also reactive, giving rise to isomeric heptadienoic acids substituted at positions 7 or 5 (generally in *ca.* 80:20 ratio) by coupling of one of the two ends of the allylic system with the terminal carbon atom of but-3-enoic acid.

Preliminary tests on other metal complexes indicate that $Rh(PPh_3)_3Cl$ in $CHCl_3$ at room temperature gives predominantly the 3,6-isomer (95% of the product of rearrangement; 15 mol of the 3,6-isomer and 2 mol of its allyl esters per mol of complex).

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[1] G. P. Chiusoli, *Accounts Chem. Res.*, 1973, **6**, 422 and references cited therein.