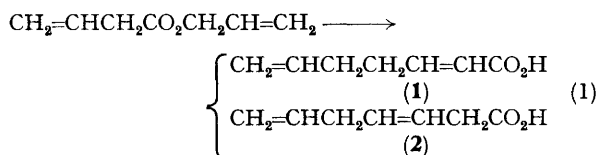


Transition Metal-catalysed Rearrangement of Allyl But-3-enoate to Hepta-2,6-dienoic or Hepta-3,6-dienoic Acids

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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)].



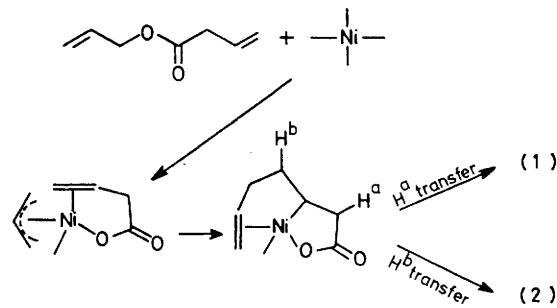
This rearrangement easily occurs at room temperature using nickel(0) complexes with phosphines or phosphites. It is highly selective (for allyl esters of but-3-enoic acid and not for those of but-2-enoic or pent-4-enoic acids) and regioselective (only the C atom of the double bond of the but-3-enoic 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)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%).

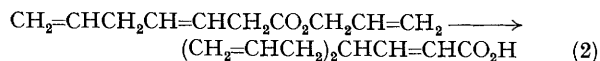
The use of different phosphorus-containing ligands also influences the 2,6:3,6 ratio. The data available so far suggest that the ability to dissociate plays a major role in determining this ratio, bulky phosphines and phosphites giving the highest value [from 14:1 with tri-*o*-tolyl phosphite to 0.8:1 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)].



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 $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ 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.