

A New Insertion Reaction. Preparation of But-3-enylsuccinic Acid by Carbonylation of Allyl Halides with Double Bond Insertion

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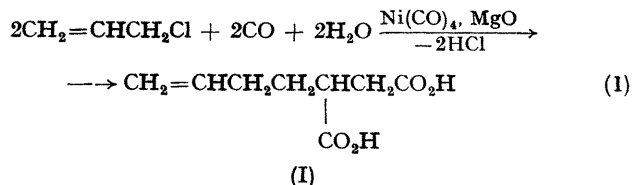
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Summary A new catalytic synthesis is described, involving carbonylation of allyl halides on tetracarbonylnickel and insertion of an olefinic double bond between the allyl and carbon monoxide groups.

It is known that allyl halides can be carbonylated on nickel catalysts in the presence of acetylene, the latter being inserted between the allyl and carbon monoxide groups.¹ Analogous insertions of butadiene on nickel² (in a copolymerization reaction with carbon monoxide) and palladium catalysts³ have been reported. The insertion of olefinic double bonds has been described only in the case of the strained olefin norbornene.⁴ We now report a new insertion reaction on nickel, involving the double bond of allyl halides.

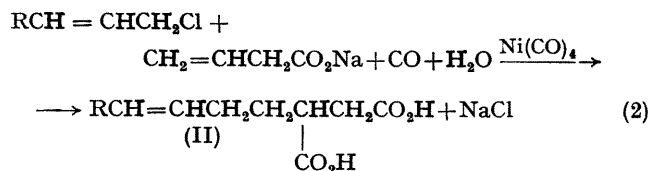
The latter are treated with tetracarbonylnickel in acetone-water solution at 40–60° in the presence of a neutralizing agent. But-3-enylsuccinic acid¹ (ca. 60%) is formed as shown in equation (1). But-3-enoic acid is

obtained in low yield but is the main product under slightly different conditions and in the absence of the neutralizing agent. However but-3-enoic acid appears to be the intermediate in this reaction, since compound (I) and its



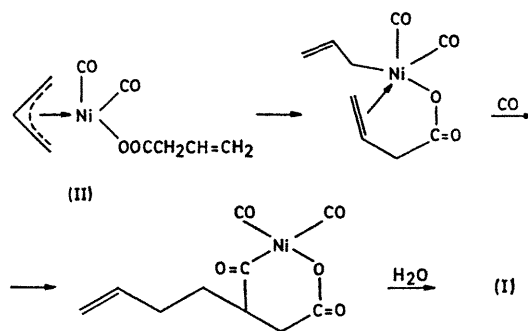
homologues can be obtained by treating allyl halides and their homologues with sodium but-3-enoate under the conditions described [equation (2)]. Only $\beta\gamma$ -unsaturated acids are reactive under the conditions tried so far. The site of addition of the allyl group to the double bond is specific. Less than 1% of allylglutaric acid (corresponding to a reversed addition of the allyl group and carbon monoxide

to the double bond) has been found in the product of the reaction of allyl chloride with tetracarbonylnickel.



We believe that the intermediate in this curious self-insertion reaction of allyl halides is a penta-co-ordinated⁵ π -allyldicarbonylnickel but-3-enoate (II) (see Scheme). On passing to the σ -form the allyl group makes a co-ordination site available to the double bond of the but-3-enoic group, thus meeting the steric requirement of the insertion reaction. This is supported by the fact that allyl but-3-enoate and tetracarbonylnickel react in acetone-water at

50° giving a limited but significant amount of but-3-enylsuccinic acid.



SCHEME

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² L. Porri, G. Natta, and M. C. Gallazzi, *Chimica e Industria*, 1964, **46**, 428; *J. Polymer Sci., Part C, Polymer Symposia*, 1967, 2525.

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⁴ M. C. Gallazzi, L. Porri, and G. Vitulli, Abstracts of papers presented at the Xth Congress of Italian Chemical Society, Padova, 17-21 June, 1968, Sec. XVI-2.

⁵ F. Guerrieri and G. P. Chiusoli, *J. Organometallic Chem.*, 1968, **15**, 209.