# Nickel-catalysed Olefin Insertion Reactions

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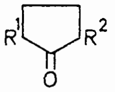
*Summary* Insertion of olefins between an allyl group and carbon monoxide gives acids or esters in the presence of water or alcohols, respectively.

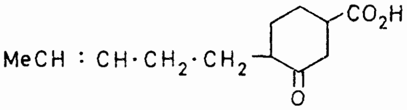
We have extended our studies[1,2] on insertion reactions with olefins and have found that under pressure ethylene undergoes reactions of type (1) in protic solvents at 40—80°. Thus, reaction (1) when carried out in aqueous acetone at 30 atm and 45° gave 42% of the acid (based on the chloride). Pent-3-enoic acid and coupling products from the but-2-enyl group were also obtained. In reactions with higher olefins, the percentage of insertion product fell to 2—4%, whilst products of type (I) increased.

$$\begin{array}{c}\mathrm{MeCH{:}CH{\cdot}CH_2Cl + CH_2{:}CH_2 + CO + H_2O} \\ \downarrow \mathrm{Ni(CO)_4} \\ \mathrm{MeCH{:}CH[CH_2]_3{\cdot}CO_2H + HCl}\end{array} \qquad (1)$$

With hexa-1,5-diene formation of an unsaturated cyclopentanone takes place much more easily. Acid (II) and a little ketone (III) are obtained from allyl chloride. This reaction is general for allylic halides and is strongly favoured by the presence of $KPF_6$, $SnCl_2$, or KF, the function of which is probably to facilitate the chelation of hexadiene on the nickel complex. Yields of acid were in the range 10—40%.



(I)–(V)



(VI)

| | $R^1$ | $R^2$ |
|---|---|---|
| (I) | $HO_2C(Me)CH$ | Alkyl group |
| (II) | $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$ | $HO_2C{\cdot}CH_2$ |
| (III) | $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$ | Me |
| (IV) | $MeCH{:}CH{\cdot}CH_3{\cdot}CH_2$ | $HO_2C{\cdot}CH_2$ |
| (V) | $HO_2C(Me)CH$ | $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$ |

Substituents on the terminal carbon of the allyl group cause formation of different products, depending on whether the cyclization occurs on the substituted or on the unsubstituted double bond. Thus, when the substituent is the methyl group, products (IV) — (VI) are formed. A ratio (IV):(V):(VI) = 72:27:1 was obtained in aqueous acetone in the presence of stannous chloride at 45°. Substituents on the carbon atoms of the 1,5-diene double-bond strongly retard the reaction.

The distance between the two double bonds of the diene is critical as evidenced by the behaviour of penta-1,4-diene, hepta-1,6-diene, and octa-1,7-diene under the same conditions of reaction as the hexadiene. The three compounds react as simple olefins with the involvement of only one double-bond. The reaction has also been obtained starting with bis-π-allyl nickel halide. It is likely to involve a cationic allylnickel complex containing a diene as chelating ligand.

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[1] G. P. Chiusoli and S. Merzoni, *Chem. Comm.*, 1971, **522**; G. P. Chiusoli, G. Cometti, and S. Merzoni, *Organometallic Chem. Synth.*, 1972, **1**, 439, G. P. Chiusoli, XXIIIrd Int. Cong. Pure Appl. Chem. Boston 1971, Special Lecture, vol. 6, p. 169, Butterworths, London.

[2] M. C. Gallazzi, L. Porri, and G. Vitulli, Abstracts of papers presented at the X Congress of the Italian Chemical Society, Padova, 17–21 June 1968, Sec. XVI-2; M. C. Gallazzi, T. L. Hanlon, G. Vitulli and L. Porri, *J. Organometallic Chem.*, 1971, **33**, C45.