The Preparation of π-Allyl Nickel Halides from Nickel Vapour

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Summary Condensation of nickel vapour with allyl bromide or chloride at −196° gives gram quantities of the corresponding π-allyl nickel halide.

A number of syntheses of π-allyl nickel halides from allyl halides is known.[1] However, most of those which give good yields require that other organo-nickel complexes are first prepared. We now report a direct preparation of π-allyl nickel bromide or chloride by condensation of nickel vapour with the corresponding allyl halide at −196°.

About 1·5 g of nickel was vaporized at 1550° over 30 min from a resistively heated alumina-coated molybdenum wire spiral[2] inside an evacuated 200 mm diameter glass vessel which was partly immersed in liquid nitrogen. About 20 g of the allyl halide was simultaneously vaporized into the vessel and condensed with the nickel vapour on the cold walls. During this co-condensation, the pressure in the vessel was below 2×10^{-4} Torr so that few gas phase intermolecular collisions occurred.

When the nickel had vaporized, the vessel was warmed to room temperature and the excess allyl halide was pumped off. The vessel was then warmed to 70° and the volatile π-allyl nickel halide pumped out into an adjoining cooled trap. The product was identified by its mass and i.r. spectra.

The π-allyl nickel bromide thus obtained was essentially pure; 2·7g of the compound were isolated, a 60% yield based on nickel vapour. The π-allyl nickel chloride was obtained in about 75% yield but it was contaminated by 1–2% of a complex mixture of C_{10}–C_{15} hydrocarbons. The residue in the vacuum vessel from the reaction with either allyl bromide or chloride was an involatile dark oil with only trace amounts of metallic nickel.

Under similar experimental conditions, nickel vapour was condensed with bromoethane at −196°. The volatile products subsequently isolated were a mixture of C_2H_4, C_2H_6, and n-C_4H_{10} in a 1 : 1 : 6 mol ratio. In this case, the residue in the vacuum vessel contained much free nickel together with a small amount of nickel(II) bromide. The total yield of hydrocarbons was only 10% based on the nickel vapour. No reaction was observed when nickel vapour was condensed with 1,3-dichloropropane.

Thus, nickel atoms do not always insert into or break carbon–halogen bonds in low-temperature reactions. The high efficiency of the reactions with allyl halides may be due to initial bonding of nickel to the unsaturated moiety.

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[1] G. Wilkie *et al.*, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[2] P. L. Timms, *J. Chem. Soc.* (*A*), 1970, 2526.