Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

1,4-DIALLYL-*cis,cis*-1,3-BUTADIENES FROM π-ALLYLNICKEL COMPLEXES, ALLYL HALIDES, AND ACETYLENE

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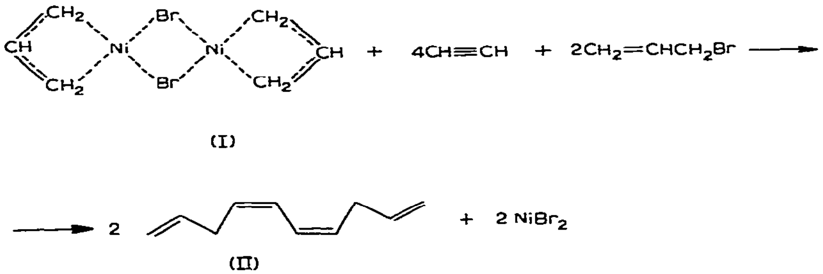
(Received June 13th, 1969)

In the effort to clarify the mechanism of acetylene insertion in the reactions of allylic halides with acetylene and carbon monoxide[1,2] we examined the behaviour of π-allylic complexes of nickel [such as (I) and its homologs] in the presence of acetylene. In previous work[3] we showed that acetylene easily polymerizes in a benzene solution of (I). By using an excess of allylic halides along with (I) and acetylene we now succeeded in obtaining a reaction involving only one molecule of acetylene per allylic group. 1,4-Diallyl-*cis,cis*-1,3-butadienes are formed according to the following (simplified) equation:



The reaction is carried out at room temperature and atmospheric pressure, simply by adding acetylene to a solution of (I) or its homologs and of an allyl halide in benzene, toluene, or acetonitrile, or their mixtures.

The products are rather unstable and tend to polymerize and so could be isolated only in a few percent yield. In the case of the dicyclohex-2-enyl derivative, however, a 25% yield was obtained.

EXPERIMENTAL

Type I complex (12 mMol) is dissolved in 150 cc of benzene under argon. The dark red solution is cooled to 5–6°, 25 mMol of an allylic bromide are added, and acetylene is introduced with stirring. Nickel bromide begins to separate, and usually after 35–45 min most of the nickel has precipitated as nickel bromide, leaving a clear yellow solution. The flow of acetylene is stopped at this point (30 mMol) and the reaction mixture is set aside for 2 h. Aqueous/methanolic hydrogen chloride is then added, the benzene layer is washed repeatedly with water and cooled to 0°, so that some of the benzene can be removed as a solid. The products are separated by distillation under high vacuum or by preparative gas chromatography. They are generally very unstable and even during the reaction rapidly polymerize to liquid and solid products. 1,4-Diallyl-*cis,cis*-1,3-butadiene and 1,4-dimethallyl-*cis,cis*-1,3-butadiene were isolated as colourless liquids by preparative gaschromatography (polyethylene glycol succinate ester on chromosorb, column length 2 m, carrier gas He, 130°). 1,4-Dicyclohex-2-enyl-*cis,cis*-1,3-butadiene was distilled at 100–110° (bath temperature)/0.005 mm; 1.2 g of it (containing bicyclohex-2-enyl as impurity) could be isolated by distillation from the reaction of 5.3 g of π-cyclohex-2-enylnickel bromide. The structures of the products were determined by elemental analysis, hydrogenation to saturated hydrocarbons and IR, UV and NMR spectroscopy. The characteristic IR absorptions of *cis*-dienes in the region 700-750 cm^{-1} and the UV absorptions in the region 237-240 mμ are useful identification tests.

The dimethallyl derivative exhibits the simplest IR and NMR spectra. The IR spectrum is free from absorptions in the region 900-1000 cm^{-1}. The NMR spectrum in $CDCl_3$ reveals two multiplets centered at τ 3.67 and 4.53 ppm, with coupling constants consistent with a *cis,cis*-butadiene structure. The spectra of the diallyl and dicyclohexenyl derivatives are more complex but it is still possible to detect a distinct multiplet at τ 3.67 and 3.75 ppm respectively[4], indicating the structure is the same as that of the dimethallyl derivative.

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