Nickel Complex-catalysed Reactions of Butadiene with Amines

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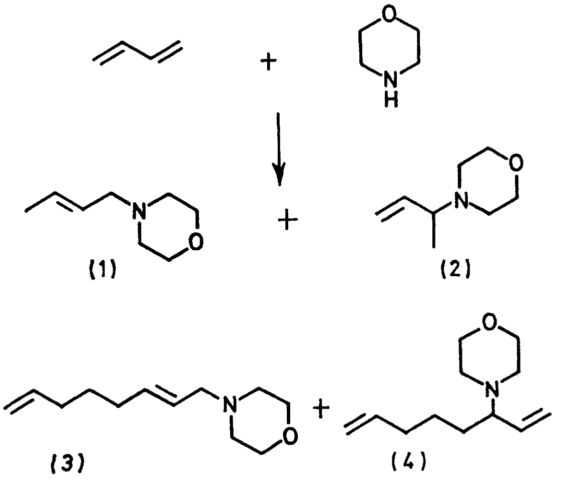
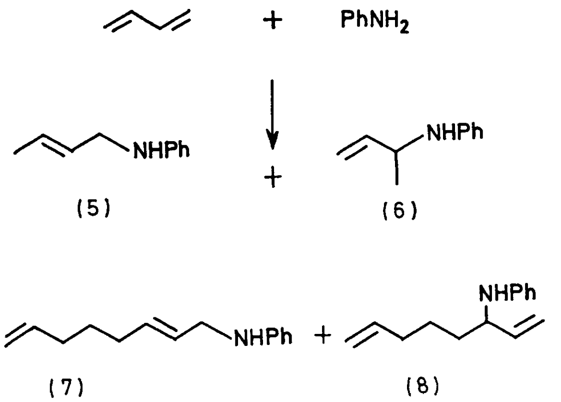
Summary Octadienyl and butenyl substituted amines have been prepared by reaction of primary and secondary amines with butadiene catalysed by nickel(0) complexes.

A NUMBER of palladium complex-catalysed reactions of active-hydrogen compounds with buta-1,3-diene have been reported. Tertiary phosphine complexes of palladium(0) have been shown to catalyse the reaction of buta-1,3-diene with methanol and phenol to give 1-methoxyocta-2,7-diene and 1-phenoxyocta-2,7-diene, respectively.[1] Similar reactions have been demonstrated with primary and secondary amines,[2] carboxylic acids,[2,3] and active-methylene and -methine compounds.[4]

Similar reactions with nickel(0) complexes would have obvious advantages but, whereas dimerisation and trimerisation of butadiene have been studied in detail,[5] only telomerisation reactions with alcohols have been reported, varying results were obtained Whereas methanol gave a mixture of butenyl and octadienyl ethers, ethanol gave a more efficient formation of octadienyl ethers but with a lower conversion of butadiene No reaction was found with isopropyl and t-butyl alcohols [6] We now report that alkylation of primary and secondary amines can be carried out in good yields by reaction with butadiene catalysed by nickel(0) complexes





Morpholine (8·70 ml, 0·10 moles), butadiene (23 ml, 0·30 moles), nickel acetylacetonate (400 mg), phenyldi-isopropoxyphosphine (500 mg), and sodium borohydride (5 mg) were heated in a sealed tube at 100° for 14 h The morpholine was totally converted into a mixture of amines (1) (32%), (2) (15%), (3) (51%), and (4) (2%) 10% of the reaction product consisted of octa-1,3,7-triene, vinylcyclohexene, and cyclo-octa-1,5-diene (in the ratio 2 : 5 : 2) The products were identified on the basis of their mass and n m r spectra † Similarly, reaction of di-n-propylamine with butadiene gave a 60% conversion into a mixture of products analogous to (1—4) in amounts 54%, 13%, 24%, and 9%, respectively ‡

A number of primary amines have also been treated with butadiene In 14 h at 100°, aniline gave a 50% conversion into a mixture of (5) (15%), (6) (56%), (7) (21%), and (8) (8%) n-Butylamine was even more reactive, together with products analogous to (5—8), 12% of the dialkylated amine (with an octadienyl and butenyl group) was also produced In this respect the greater basicity of n-butylamine compared to aniline can be seen to be important in determining the course of the reaction

These reactions depend upon the ability of the alkoxyphosphine to reduce the Ni^{II} salt to a Ni^0 species,[7] other phosphines such as triphenylphosphine do not accomplish this result The presence of amines has, in fact, been suggested to be beneficial to the dimerisation of butadiene catalysed by Ni^0 complexes [8,9] In one report a small amount of amine alkylation was observed and it was suggested that this increased with increase in temperature [9] It is evident that the present method of *in situ* generation of the Ni^0 complex yields a species which favours amine alkylation over butadiene dimerisation Differing methods of generation of Ni^0 complexes can therefore be seen to markedly affect the course of butadiene reactions

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† Separation of the products was achieved by fractional distillation and g l c The structure of (4) was assigned on the basis of a g l c -mass spectrum of a mixture of (3) and (4) obtained from fractional distillation The double bonds in (1) and (3) have been assigned *trans* on the basis of their i r spectra

‡ Octa-1,3,7-triene, vinylcyclohexene, and cyclo-octa-1,5-diene, from the dimerisation of the excess of butadiene were obtained in all these reactions Thus, the total reaction product from aniline, n-butylamine, and di-n-propylamine consisted of 53%, 66%, and 43% of hydrocarbon, respectively

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