Nickel-catalysed Reactions of Allene and Active Hydrogen Compounds

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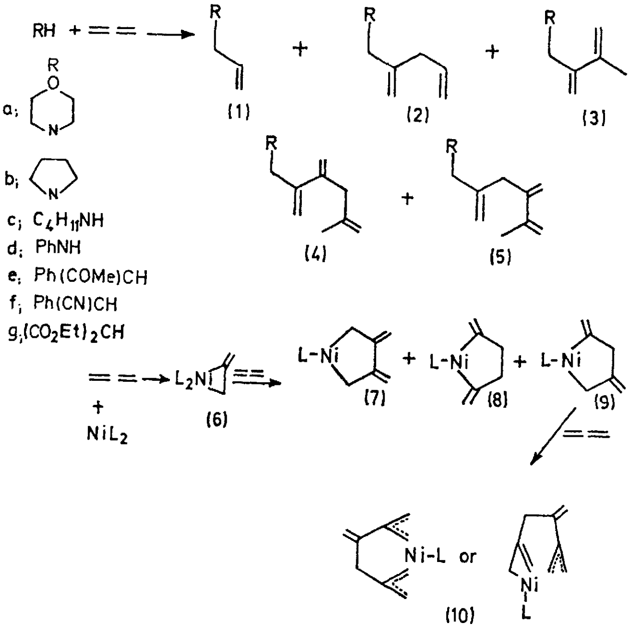
Summary The reaction of allene and amines or active methylene compounds with a nickel(0) catalyst has been shown to yield an adduct consisting of 3 mol of allene and 1 mol of active hydrogen compound as major product.

Although there are many examples of oligomerisation reactions of allene, only two reports of telomerisation with other reagents have appeared.[1,2] We report the reactions of allene with primary and secondary amines and active methylene compounds in the presence of nickel(0) complexes which give a series of novel adducts and yield information on the nature of intermediates in nickel-catalysed allene reactions.



In a typical reaction, morpholine (50 mmol), allene (150—180 mmol), nickel bromide (1 mmol), and phenyldi-isopropoxyphosphine (1 mmol) in ethanol (2·5 ml) were heated in a sealed tube at 100° for 1 h. The morpholine was totally converted into a mixture of (**1a**) (trace), (**2a**) (1%), (**3a**) (22%), (**4a**) (72%), and (**5a**) (5%).† A small part of the reaction mixture consistsd of cyclic allene oligomers. Similarly, reaction of pyrrolidine and allene gave a 63% conversion into (**1b**) (7%), (**2b**) (10%), (**3b**) (36%), (**4b**) (43%), and (**5b**) (4%). Primary amines behave in an analogous way; under the same conditions n-butylamine gave an 83% conversion into (**1c**) (trace), (**2c**) (21%), (**3c**) (33%), (**4c**) (33%), and (**5c**) (9%) (a small amount of dialkylated products was also obtained).

With nickel acetylacetonate, phenyldi-isopropoxyphosphine, sodium borohydride, ethanol, and sodium phenoxide as co-catalyst, reaction for 16 h at 75° with benzyl methyl ketone, benzyl cyanide, and diethyl malonate gave the products (**3e**) (14%), (**4e**) (63%), and (**5e**) (23%); (**3f**) (25%), (**4f**) (60%), and (**5f**) (15%); (**3g**) (trace), (**9g**) (100%), and (**5g**) (trace) in 18, 20, and 21% yields, respectively.‡ This relative lack of reactivity of active methylene compounds with respect to amines has also been noted in the nickel catalysed reaction of active hydrogen compounds with butadiene.[3]

It is evident that these reactions are occurring *via* a nickel(0) species, formed from the reduction of a nickel(II) salt by phenyldi-isopropoxyphosphine.[4] With the exception of the reaction with n-butylamine, the major products in all cases result from addition of 3 mol of allene and 1 mol of amine or active methylene compound. These products arise from addition to (**10**) with preferential reaction at the π-allyl adjacent to the *exo*-methylene group. The intermediate (**10**) has been isolated[5,6] and its structure assigned by *X*-ray studies.[7] Formation of (**2**) can be seen to result from attack at the allylic carbon atom adjacent to nickel in the intermediate (**9**). Similarly, attack on an intermediate of structure (**7**) accounts for formation of (**3**). Both (**9**) and (**7**) have been invoked together with the dimeric intermediate (**8**) in the oligomerisation of allene with (triphenylphosphine)$_2$nickel.[8] The small amount of (**1**) obtained appears to be formed from (**6**) or a simple π-complex formed between 1 mol of allene and the nickel catalyst.

It is clear that the stability of (**10**) is the controlling feature in these reactions[5,9] since formation of trimeric allene adducts are favoured in contrast to rhodium- and palladium-catalysed processes where dimeric allene adducts are produced.[2] Isolation of 1:1 and 2:1 allene-active hydrogen compound adducts, together with the 3:1 adduct in the present reaction is consistent with the interception of a series of intermediates formed by stepwise addition of allene on the nickel–phosphine catalyst.

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† The spectral data are fully consistent with the assigned structures.

‡ Nickel bromide cannot be used with active methylene compounds due to polymerisation occurring.

[1] G. D. Shier, *J. Organometallic Chem.*, 1967, **10**, 15.

[2] D. R. Coulson, Proc. 163rd A.C.S. Nat. Meeting, Boston, Massachusetts, April 9—14, 1972, p. 52.

[3] R. Baker, A. H. Cook, and T. N. Smith, *Tetrahedron Letters*, 1973, 503.

[4] A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, 1969, **3**, 8.

[5] S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Comm.*, 1971, 863.

[6] M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1972, **11**, 136.

[7] B. L. Barnett, C. Kruger, and Y.-H. Tsay, *Angew. Chem. Internat. Edn.*, 1972, **11**, 137.

[8] R. J. De Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.

[9] S. Otsuka, A. Nakamura, T. Yamagata, and K. Tani, *J. Amer. Chem. Soc.*, 1972, **94**, 1037.