

## Nickel-catalysed Reactions of Allene and Active Hydrogen Compounds

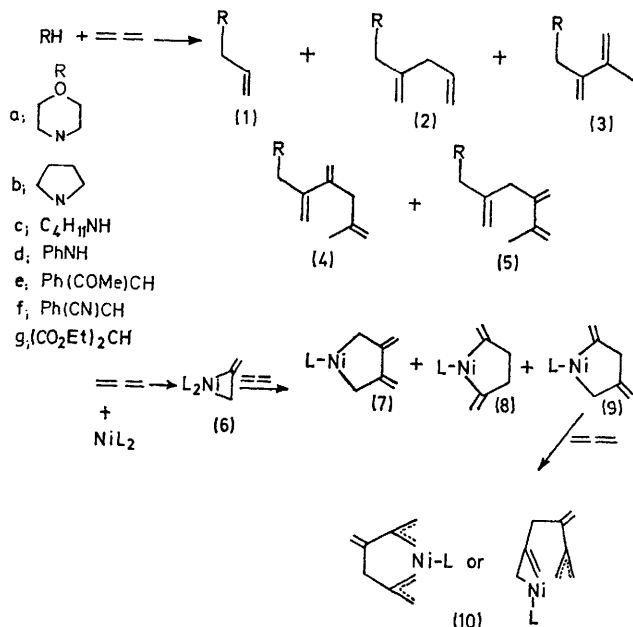
By RAYMOND BAKER\* and ALAN H. COOK

(*Department of Chemistry, The University, Southampton SO9 5NH*)

**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.<sup>1,2</sup> 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 phenyldiisopropoxyphosphine (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 consisted 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).

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

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

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<sup>3</sup> R. Baker, A. H. Cook, and T. N. Smith, *Tetrahedron Letters*, 1973, 503.

<sup>4</sup> A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, 1969, **3**, 8.

<sup>5</sup> S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Comm.*, 1971, 863.

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<sup>7</sup> B. L. Barnett, C. Kruger, and Y.-H. Tsay, *Angew. Chem. Internat. Edn.*, 1972, **11**, 137.

<sup>8</sup> R. J. De Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.

<sup>9</sup> S. Otsuka, A. Nakamura, T. Yamagata, and K. Tani, *J. Amer. Chem. Soc.*, 1972, **94**, 1037.

With nickel acetylacetonate, phenyldiisopropoxyphosphine, 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.<sup>3</sup>

It is evident that these reactions are occurring *via* a nickel(0) species, formed from the reduction of a nickel(II) salt by phenyldiisopropoxyphosphine.<sup>4</sup> 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  $\pi$ -allyl adjacent to the *exo*-methylene group. The intermediate (10) has been isolated<sup>5,6</sup> and its structure assigned by X-ray studies.<sup>7</sup> 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)<sub>2</sub>nickel.<sup>8</sup> The small amount of (1) obtained appears to be formed from (6) or a simple  $\pi$ -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<sup>5,9</sup> since formation of trimeric allene adducts are favoured in contrast to rhodium- and palladium-catalysed processes where dimeric allene adducts are produced.<sup>2</sup> 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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