

Stereochemistry and Mechanism of the Nickel-catalysed Hydrocyanation of Conjugated Dienes

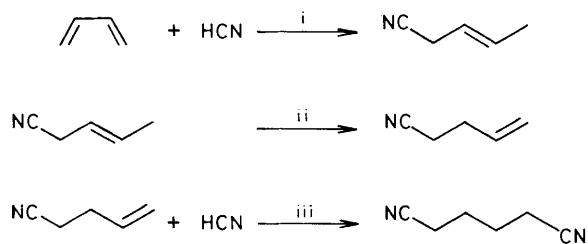
Jan-E. Bäckvall* and Ove S. Andell

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Nickel-catalysed addition of deuterium cyanide to cyclohexa-1,3-diene was shown to occur with *cis* stereochemistry, indicating that a *cis*-migration of co-ordinated cyanide takes place in an intermediate π -allylnickel complex.

The adiponitrile process, developed at Du Pont more than ten years ago, has become one of the many successful industrial processes utilizing homogeneous catalysis.¹ In this process two molecules of hydrogen cyanide are added to butadiene and the reaction proceeds in three discrete steps (Scheme 1).

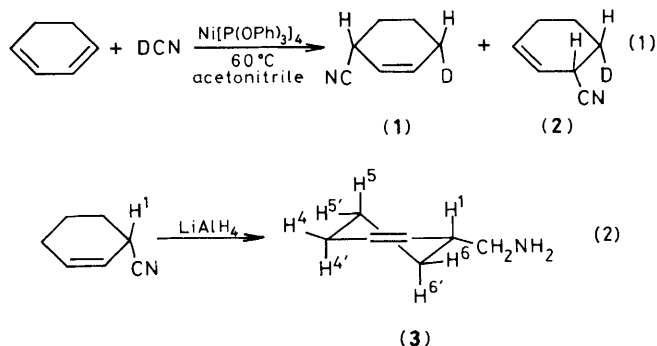
Although hydrocyanation of both mono-olefins and conjugated dienes using nickel and palladium catalysts has been known for some time,²⁻⁴ it is only of late that the mechanism of these reactions has attracted attention.⁵⁻⁸ We recently showed that the nickel-catalysed addition of hydrogen cyanide to mono-olefins occurs *cis* (cf. step iii, Scheme 1).⁵ The analogous addition to 1,3-dienes (cf. step i, Scheme 1) is generally believed to proceed *via* a nickel hydride addition to give a π -allylnickel complex, followed by attack by cyanide on the allyl group.^{6,7} We report here that deuterium cyanide adds *cis* to cyclohexa-1,3-diene in the presence of a nickel triphenyl phosphite catalyst, indicating that a *cis*-migration of co-ordinated cyanide takes place in an intermediate π -allylnickel complex.

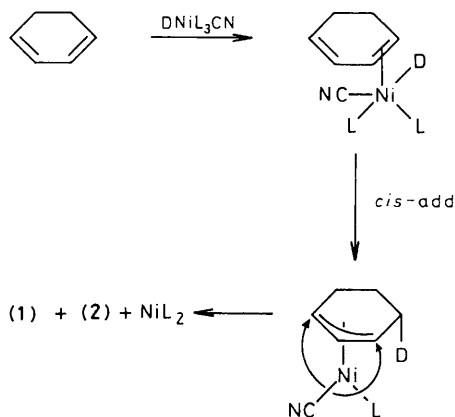
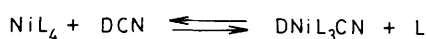


Scheme 1. L = P(OAr)₃, i, NiL₄; ii, isomerisation, iii, NiL₄.

Reaction of cyclohexa-1,3-diene with HCN in the presence of 2 mol % of Ni[P(OPh)₃]₄ with some added P(OPh)₃ produced cyclohex-2-enecarbonitrile with high selectivity (*ca.* 15 turnovers). The same reaction using DCN afforded the monodeuteriated nitriles (1) and (2) in approximately equal amounts [equation (1)]. The mass spectrum of the mixture of (1) and (2) is consistent with deuterium occupying the 4- and 6-positions. It was not possible from the ¹H n.m.r. spectrum of the deuteriated nitriles (1) and (2) to establish whether deuterium and cyanide are *cis* or *trans* to one another, since none of the crucial protons in the 4- and 6-positions separate well enough from the rest of the protons.

We therefore reduced the cyano groups in (1) and (2) to CH₂NH₂ groups, which would be expected to lock the systems in one conformation [equation (2)].⁹ The ¹H n.m.r. spectrum of undeuteriated amine (3) showed a good separation of the

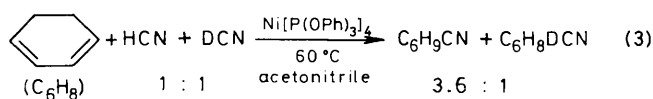


Scheme 2. L = P(OPh)₃.

protons, and from decoupling experiments and the magnitude of the coupling constants the following assignment was made: (200 MHz, CDCl₃) δ 1.29 (6'-H, $J_{1,6'}$ 8.9, $J_{5,6'}$ 11.4, $J_{5',6'}$ 3.0, $J_{6,6'}$ -12.9 Hz), 1.54 (5-H), 1.73 (5'-H), 1.79 (6-H), 1.99 (4-H, 4'-H), 2.12 (1-H). The ¹H n.m.r. analysis of the deuteriated amines obtained from (1) and (2), showed that the signals of 6'-H at δ 1.29 had only about half the intensity of one proton. Further, the 6'-H resonance was unchanged from that of the undeuteriated parent compound (3). In contrast, the patterns of the protons 6-H, 5-H, 5'-H, and 1-H were much changed owing to deuterium couplings. This indicates that *ca.* half of the deuteriated amine is (3, 6'-H = D), which requires that deuterium and cyanide are *cis* to one another in (2). The integrated area at δ 1.99 (4-H, 4'-H) in the ¹H n.m.r. spectrum of the deuteriated amine is *ca.* 1.5, indicating that the other half of the product has deuterium in the 4-position.

A probable mechanism of the reaction is shown in Scheme 2. Oxidative addition of DCN to NiL₄ [L = P(OPh)₃] generates the active DNiL₃CN.^{7,10} Co-ordination of one of the double bonds followed by a *cis*-migration of the co-ordinated deuteride produces a π-allylnickel complex. It is well known that nickel hydrides and other transition metal hydrides add *cis* to olefins.^{11,12} A *cis*-migration of the co-ordinated cyanide to the co-ordinated allyl group would then give (1) and (2). The fact that (1) and (2) are formed in approximately equal amounts confirms the intermediacy of a π-allylnickel complex.

In the addition of DCN to 1-deuterio-3,3-dimethylbut-1-ene we previously observed a considerable amount of HCN addition.⁵ Even if one takes into account the HCN that is generated through exchange with the olefin, the relative amount of HCN addition product was too high and suggests an isotope effect.† In the diene system studied here no exchange



occurs, the recovered cyclohexa-1,3-diene being completely undeuteriated according to its mass spectrum. It was therefore possible to determine the isotope effect in the addition to cyclohexa-1,3-diene by a competitive experiment using HCN:DCN in a 1:1 ratio. Analysis of the products from such an experiment [equation (3)] by mass spectroscopy, shows a ratio of HCN-adduct:DCN-adduct of 3.6:1, indicating a deuterium isotope effect of 3.6 ± 0.4 .

The present study establishes *cis* nucleophilic attack by cyanide on π-allylnickel complexes. Nucleophilic addition to π-allylnickel complexes has been studied in both catalytic and stoichiometric systems,^{11b,13-15} and previous stereochemical studies have shown *trans*-attack by amine^{11b} and *cis*-attack by methyl and phenyl anions.¹⁴

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† A typical product ratio was Bu^tCH₂CHDCN:Bu^tCHDCHDCN:Bu^tCD₂CHDCN = 15:70:15. The recovered olefin was Bu^tCH=CHD:Bu^tCD=CHD = 70:30. DCN was used in a tenfold excess to olefin.