Insertion of Isocyanides into Bis-π-allylnickel Complexes and the Formation of (±)-Muscone†

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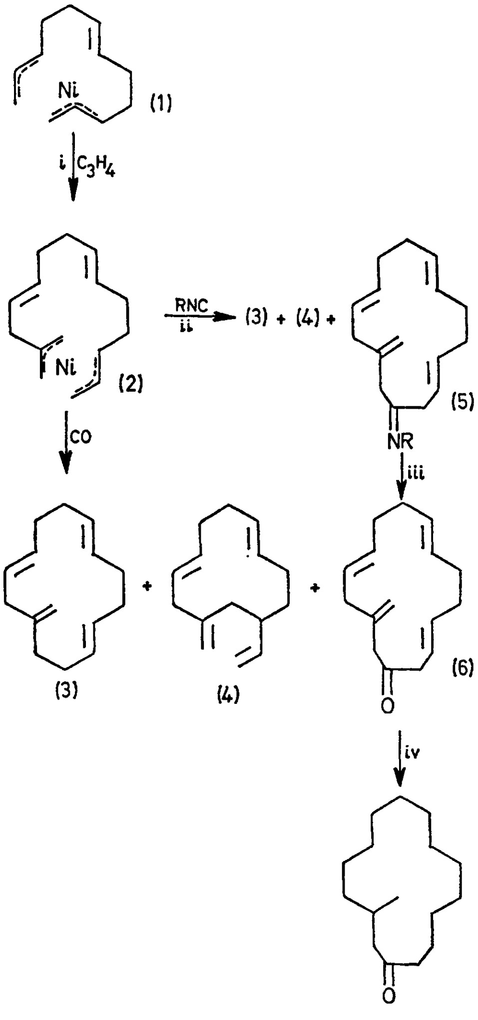
Summary Reaction of the bis-π-allylnickel complex formed from butadiene and allene has been shown to undergo insertion with alkyl isocyanides to give a cyclic imine which on hydrolysis and hydrogenation yields (±)-muscone in good yield.

Reaction of the dodecatrienyl nickel complex (**1**) with allene, followed by carbon monoxide at 0—10° yields the hydrocarbons (**3**) and (**4**) together with a small amount of the ketone (**6**), from which (±)-muscone may be derived by hydrogenation.[1] Insertion of isocyanide into (**1**) has been reported to give 11- and 13-membered cyclic imines.[2] We now report the reaction of (**1**) with allene followed by isocyanides to give imines from which the ketone (**6**) may be obtained by hydrolysis in good yield.

When allene from a gas reservoir is passed on to the surface of an ether solution of (**1**) [prepared from butadiene and bis(cyclo-octadienyl)nickel below 0°], under argon at −10 to −20°, a rapid uptake of the gas occurs, which is stopped after 1·5 equiv. have been absorbed. Addition of t-butyl isocyanide (5 equiv.) at −20° produces a yellow suspension of tetrakis-(t-butylisocyano)nickel and a mixture of organic products.‡ When these were chromatographed on silica, after hydrolysis with hydrochloric acid, elution with light petroleum (b.p. 30—40°) gave cyclododecatriene [from (**1**)], (**3**), and (**4**).

Further elution with light petroleum–ether (50 : 1) gave 3-methylenecyclopentadeca-5,9,13-trienone (**6**)§ followed by fractions containing a little cyclotrideca-3,7,11-trienone, the latter being formed from (**1**). On hydrogenation (Pd–C, 5%) (**6**) gave an oil with a strong musk odour, which was shown to be identical to authentic (±)-muscone. A yield of 40% of muscone based on (**1**) was obtained and the ratio of insertion in (**2**) to formation of hydrocarbon by coupling was 10 : 1.

Reaction of (**2**) with cyclohexyl, phenyl, n-butyl, isopropyl, and ethyl isocyanides produced similar products although insertion is enhanced by the smaller isocyanides. An alternative mode of insertion of cyclohexyl isocyanide into (**1**) has been observed,[2] giving the smaller, 11-membered ring with an exocyclic vinyl group whereas a 13-membered ring was obtained with t-butyl isocyanide. The alternative



Reagents: i, slight excess of allene, −20 to −10°; ii, RNC, −20°; iii; AcOH-3·5N-H_2SO_4 (1 : 1; 30%), 20°; iv, H_2, 5% Pd–C.

† B.P. provisional application 42,225/73.

‡ Alternatively 1 equiv. of isocyanide can be used, followed by an excess of potassium cyanide or carbon monoxide.

§ G.l.c. analysis indicates that more than one isomer is formed and i.r. spectra give evidence for an isomer with a *cis*-double bond.

mode of insertion into (**2**) would produce, after hydrolysis, 12-methylene-2-vinylcyclotrideca-5,9-dienone, but in no case could this product be identified. The present results therefore contrast with insertion of isocyanides into (**1**).[2] A similar preference for the larger ring has been observed in insertion of carbon monoxide into (**2**), as opposed to insertion in (**1**), when only the smaller ring is formed.[3]

Reaction of (**2**) with t-butyl isocyanide at −78° results in an increased ratio (20 : 1) of imine to hydrocarbon formed, although the rate of reaction, estimated from the rate of disappearance of the deep red colour of (**2**) and the formation of the yellow suspension, is slower than at −20°.

The effect of electron donating and accepting ligands on the competing modes of reaction was studied by addition of ligands, after insertion of allene but before the addition of t-butyl isocyanide, at −40°. Triphenylphosphine had little effect on the ratio of insertion to coupling of 10 : 1 with no ligand present; triphenyl phosphite reduced the ratio to 0·9 : 1 whereas the ratio was increased to 20 : 1 in the presence of pyridine.

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