

Insertion of Isocyanides into Bis- π -allylnickel Complexes and the Formation of (\pm)-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 (\pm)-muscone in good yield.

REACTION of the dodecatrienylnickel 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 (\pm)-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).

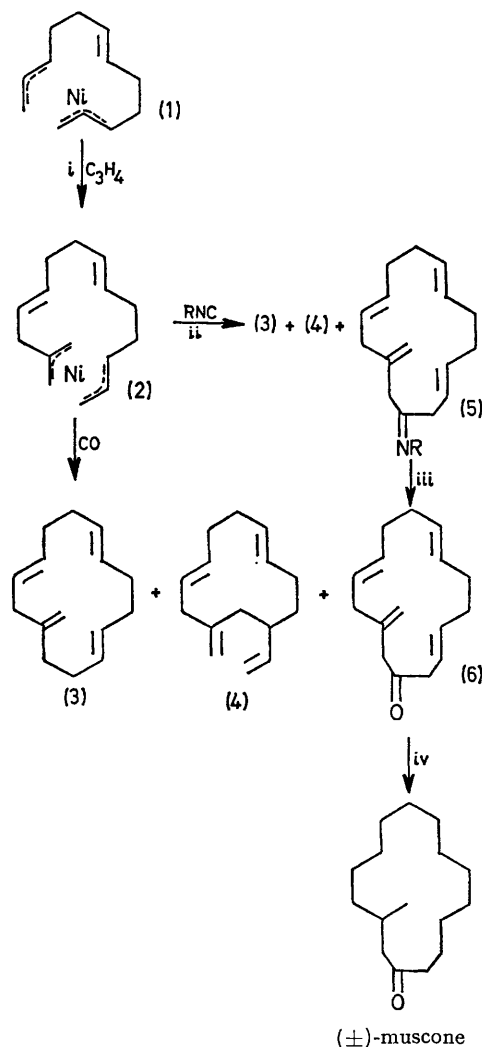
Further elution with light petroleum–ether (50:1) gave 3-methylenecyclopentadeca-5,9,13-trienone (6)[§] followed by fractions containing a little cyclotrideca-3,7,11-trienone, the latter being formed from (1). On hydrogenation (Pd–C, 5%) (6) gave an oil with a strong musk odour, which was shown to be identical to authentic (\pm)-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

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[‡] 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.



Reagents: i, slight excess of allene, –20 to –10°; ii, RNC, –20°; iii, AcOH–3.5N-H₂SO₄ (1:1; 30%), 20°; iv, H₂, 5% Pd–C.

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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