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INSERTION OF ISOCYANIDE AND CARBON MONOXIDE INTO α,ω-OCTADIENDIYLNICKEL AND AN ALLENE DERIVED BIS-$\underline{\pi}$-ALLYLNICKEL COMPLEX

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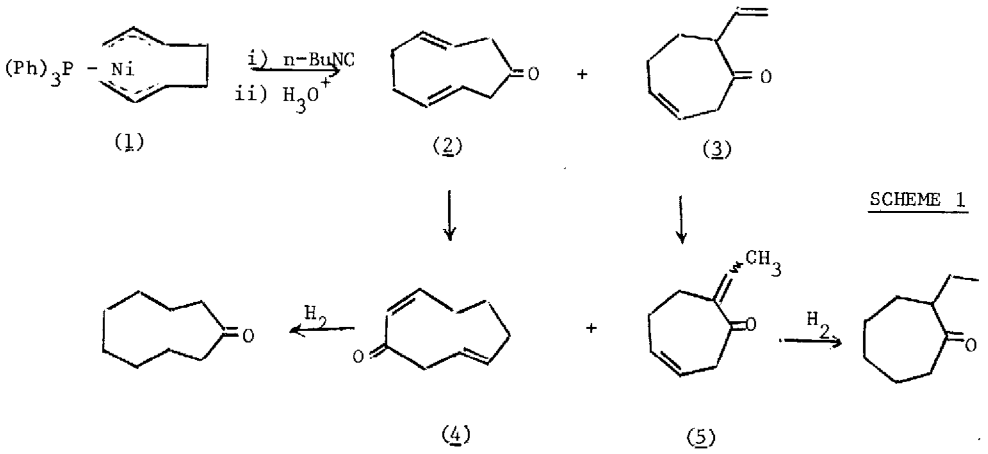
The reaction of carbon monoxide with bis-π-allylnickel complexes has been demonstrated to result in either insertion, with formation of ketones, or a coupling process to yield hydrocarbons. Thus, carbonylation of bis-π-allylnickel[1] and octadiendiylnickel above -40°[2] yields exclusively hydrocarbon products while at -60° a similar reaction with dodecatriendiylnickel afforded cyclic ketone in good yield[3]. The unpredictable nature of these reactions was confirmed by the carbonylation of a bis-π-allylnickel complex obtained by the reaction of allene with dodecatriendiylnickel; only small amounts of ketone were obtained at 10°[4]. In contrast, good yields of cyclic ketones have been obtained by the hydrolysis of imines produced by insertion of alkyl isocyanides into this same nickel complex[5] and dodecatriendiylnickel[6].

In the present communication we report the isolation of a good yield of a 1.6:1 mixture of C_9- and C_7- membered ring ketones derived from the insertion of n-butyl isocyanide into the α,ω-octadiendiylnickel complex (1). The critical effect of temperature on the carbonylation of the bis-π-allylnickel complex (6) derived from allene is also reported, together with evidence obtained for the formation of a $Ni(C_9H_{12})(CO)$ intermediate.

n-Butyl isocyanide (97 mmol) in diethyl ether (40 ml) was added dropwise to a stirred solution of α,ω-octadiendiylnickel (1) derived from $Ni(COD)_2$ (14.2 mmol), butadiene (50 mmol) and triphenylphosphine (14.2 mmol) at -78° and allowed to warm to room temperature slowly overnight. The product mixture was hydrolysed with dilute acid and the presence of a mixture of conjugated and non-conjugated ketones indicated by the infrared spectrum. G.l.c./mass spectral analysis of the mixture indicated the presence of three products in the ratio 1:0.39:0.21 each with a molecular ion M = 136. The ratio of products changed with time



SCHEME 1

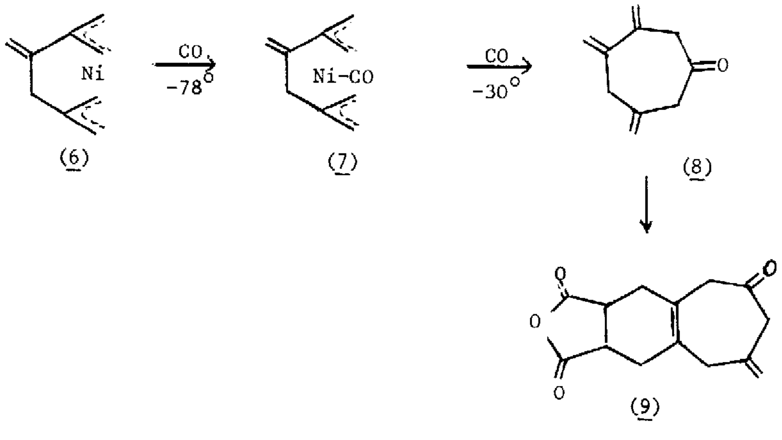
and after the mixture had been stirred with activated charcoal to remove the dark red nickel complexes, g.l.c. analysis indicated the presence of only two major products in the ratio 1:0.6. This ketone mixture (782 mg, 38% based on Ni (COD)$_2$) was separated from cyclooctadiene and other hydrocarbons by column chromatography.

A sample of one ketone obtained, although pure by g.l.c., was assigned as a 6:1 mixture of (4) and (2), δ(CCl$_4$): 4.7 - 5.4 (4H, complex m, -CH=CH-), 2.79 - 3.20 and 2.11 - 2.66 (2xm, =C-CH$_2$ -C=O, -CH$_2$ -C=C-C=O, -CH$_2$ -C=), 1.44 - 1.64 (m, -CH$_2$- in (4)). Both molecules contain four olefinic protons but only (4) contains two protons in an unconjugated -CH$_2$- group and by a comparison of the integrals of the resonances in these two regions, the 6:1 ratio could be deduced. The infrared spectrum showed a broad, strong absorption at 1710 cm^{-1} which could not confirm the presence of both conjugated and non-conjugated carbonyl groups, but two absorptions at 1655 cm^{-1} and 1630 cm^{-1} suggested the presence of both conjugated and non-conjugated carbon-carbon double bonds. In addition, absorptions at 980 cm^{-1} and 720 cm^{-1} suggested the presence of both cis and trans double bonds. An ethanolic solution of this 6:1 mixture of (4) and (2) containing 5% Pd/charcoal catalyst was stirred under hydrogen at room temperature until uptake of the gas ceased. A colourless oil was isolated and identified as cyclononanone.

A sample of the second ketone formed in the reaction was isolated by preparative g.l.c. and assigned the structure (5), ν_{max} 1695 cm^{-1}, δ(CCl$_4$): 6.72 (1H,q, J_{CH_3-CH}=7Hz, =C$\underline{H}$-CH$_3$), 5.46 - 5.56 (2H,m, -CH=CH-), 3.16 - 3.25 (2H,m, =C-CH$_2$-C=O), 2.58 - 2.70 (2H,m, -CH$_2$-C=), 2.24 - 2.31 (2H, bm,-CH$_2$-C=), 1.80 (3H,d,J_{CH_3-CH}=7Hz, =CH-CH$_3$). An ethanolic solution of (5) containing Pd/charcoal catalyst was stirred under hydrogen at room temperature overnight. Two molar equivalents of hydrogen were absorbed and a colourless oil, 2-ethylcycloheptanone, isolated.

Addition of n-butyl isocyanide to (1) at -78° has been shown therefore to yield, after hydrolysis, a 1.6:1 mixture of large and small ring ketones (scheme 1); isomerisation probably occurs during reaction and in the work up procedure. Thus while carbonylation of (1) afforded only hydrocarbon from a coupling reaction[2], the addition of isocyanide yields ketone in ca. 40% yield. This result confirms that isocyanides are more active towards insertion than carbon monoxide.

Insertion of carbon monoxide and isocyanide into the bis-π-allylnickel intermediate (6) has also been investigated. Formation of (6) by reaction of Ni(COD)$_2$ (15 mmol) with excess allene (10 ml, 150 mmol) at -30° followed by the addition of tert-butyl isocyanide (145 mmol) afforded a yellow-brown oil exhibiting a strong absorption at 1603 cm^{-1}. Although insertion to form an imine had apparently occurred, no ketone was isolated when the mixture was hydrolysed with dilute acid or base. This can be attributed to polymerisation under the hydrolysis conditions. Carbonylation of a solution (6) in diethyl ether at -30° gave (8) in yields of 50 - 80% although losses due to its ready polymerisation were found during isolation[7]. A Diels-Alder addition confirmed the presence of a diene unit in (8) since reaction with maleic anhydride in benzene afforded (9), m.p. 110-111°, ν_{max} 1830, 1775, 1710 and 1648 cm^{-1}, δ(CDCl$_3$); 4.89 and 4.98 (2H, 2xbs, -C=CH$_2$), 3.4(2H,m,methine), 2.99-3.15 (6H,m, =C-CH$_2$-C=), 2.45 (4H, bs, -CH$_2$-C=). Information on the course of this reaction has been obtained by passage of carbon monoxide into a solution of (6) at -78°. No visible change in the colour of the red solution was observed over a period of 28 hours. Infrared analysis of a portion of the reaction mixture gave no evidence for ketone formation but there was, however, a very strong absorption at 2000 cm^{-1}. This suggested the formation of a Ni-CO bond and that insertion of carbon monoxide into (6) proceeds via the formation of the intermediate complex (7). Further reaction is not observed unless the reaction mixture is warmed to -30° with further passage of carbon monoxide when insertion and formation of (8) occurs.



Thus there is clear evidence to suggest that formation of (8) proceeds via the formation of an unstable intermediate. A similar intermediate has been postulated to be formed when bis-π-allylnickel is treated with carbon monoxide below -40°[1]. Further reaction of these intermediates, one to give an insertion product and the other to give a coupled product, does not occur until the mixtures are warmed to -40°. In sharp contrast, carbonylation of the dodecatriendiylnickel complex at -60° affords C_{13} ketone in high yield[3]. It is clear that the temperature at which these carbonylation reactions are performed is highly critical but, the factors which direct the course of reaction into coupling or carbonyl insertion have still not been defined.

Acknowledgement

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