

## Insertion of Carbon Monoxide and n-Butyl Isocyanide into Bis- $\pi$ -allylnickel Intermediates derived from Reaction of $\alpha\omega$ -Octadienediylnickel and Allene

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A series of  $C_{11}$ ,  $C_{14}$ , and  $C_{17}$  bis- $\pi$ -allylnickel complexes has been formed by the sequential insertion of 3 mole equivalents of allene into  $\alpha\omega$ -octadienediylnickel. Treatment of these complexes with carbon monoxide gave mainly hydrocarbon products from a coupling reaction together with a low yield of a mixture of two dimethylene cyclotridecadienones derived from the  $C_{14}$  nickel complex. Treatment of these complexes with n-butyl isocyanide followed by hydrolysis, did not significantly increase the yields of these ketones but, in addition, a small amount of a methylene cycloundecadienone was obtained from the  $C_{11}$  nickel complex. Experiments showed that little selectivity could be obtained in the formation of the bis- $\pi$ -allylnickel complexes.

THE reaction of carbon monoxide with bis- $\pi$ -allylnickel complexes has been demonstrated to result in either insertion, with formation of ketones, or a coupling process to yield hydrocarbons.<sup>1-5</sup> Good yields of ketones have also been obtained by the hydrolysis of imines produced by insertion of alkyl isocyanides into bis- $\pi$ -allylnickel complexes. In a number of cases it has been shown that the insertion of alkyl isocyanides into bis- $\pi$ -allylnickel complexes occurs more readily than carbon monoxide. Thus, insertion of alkyl isocyanides into a bis- $\pi$ -allylnickel intermediate derived from reaction of  $\alpha\omega$ -dodecatrienediylnickel and allene has been shown to proceed in good yield,<sup>6</sup> whilst carbonylation yielded only small amounts of ketone product.<sup>7</sup> Good yields of cyclic ketones have also been obtained by the insertion of n-butyl isocyanide into  $\alpha\omega$ -octadienediylnickel followed by acid hydrolysis;<sup>8</sup> only hydrocarbons were obtained by the carbonylation of this same nickel complex.<sup>9</sup>

The present studies were initiated to obtain results to provide further understanding of the factors governing insertion reactions and to provide a comparison of the use of carbon monoxide and alkyl isocyanides in the synthesis of cyclic ketones. In a previous paper we described studies on these insertion reactions in the bis- $\pi$ -allylnickel intermediates obtained by successive insertion of allene into  $\alpha\omega$ -dodecatrienediylnickel.<sup>10</sup> In these reactions it was shown substantial amounts of ketones could be obtained by hydrolysis of the products resulting from insertion of n-butyl isocyanide; only hydrocarbons were produced by the analogous carbonylation. We now report similar studies of insertion reactions of bis- $\pi$ -allylnickel intermediates derived from  $\alpha\omega$ -octadienediylnickel and allene in which only low yields of ketones could be obtained by either carbonylation or isocyanide insertion and hydrolysis.

<sup>1</sup> P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1970, **8**, 29.

<sup>2</sup> M. F. Semmelhack, *Org. Reactions*, 1972, **19**, 115.

<sup>3</sup> R. Baker, *Chem. Rev.*, 1973, **73**, 487.

<sup>4</sup> G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkurch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151 and 157.

<sup>5</sup> B. Barnett, B. Bussemeier, P. Heimbach, P. W. Jolly, C. Kruger, I. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, **15**, 1457.

<sup>6</sup> R. Baker, R. C. Cookson, and J. R. Vinson, *J.C.S. Chem. Comm.*, 1974, 515.

### RESULTS AND DISCUSSION

*Reactions with Carbon Monoxide.*—Dried allene was distilled into an ethereal solution of  $\alpha\omega$ -octadienediylnickel (1) derived from biscyclo-octa-1,5-dienickel<sup>11</sup> (7 g, 27 mmol) held at  $-28^\circ\text{C}$  and was allowed to reflux for 2 h. The mixture was cooled to  $-78^\circ\text{C}$  and carbon monoxide passed in overnight while the mixture was allowed to warm slowly to room temperature. The product mixture was fractionally distilled under reduced pressure and preparative g.l.c. enabled pure samples of three products to be isolated. These were identified by mass spectroscopy to be a  $C_{11}$  and two  $C_{14}$  cyclic hydrocarbons.

The  $C_{11}$  hydrocarbon was assigned the structure (7);  $\delta(\text{CCl}_4)$ : 5.15—5.95 (2 H, complex m,  $-\text{CH}=\text{CH}_2$ ), 5.01 and 4.89 (4 H, 2  $\times$  complex m,  $\text{CH}=\text{CH}_2$ ), 4.62 (2 H, m,  $\text{C}=\text{CH}_2$ ), 1.97—2.47 (6 H, complex m,  $4-\text{CH}_2-\text{C}=\text{}$  and 2 methine), 1.67 (2 H, m,  $\text{CH}_2$ ). I.r. spectral analysis confirmed the presence of a vinyl group by the strong absorptions at 992 and 910  $\text{cm}^{-1}$ . The two  $C_{14}$  hydrocarbons isolated were assigned the structures (8) and (9). These similar structures afforded n.m.r. spectra that were too similar for definitive assignment of each structure to a particular spectrum to be made; their characteristics were  $\delta(\text{CCl}_4)$ : 5.18—5.38 (4 H, m,  $\text{CH}=\text{CH}$ ), 4.58—4.89 (4 H, m,  $\text{C}=\text{CH}_2$ ), 2.68—2.80 (4 H, m,  $=\text{C}-\text{CH}_2-\text{C}=\text{}$ ), 2.0—2.24 (8 H, m,  $\text{CH}_2-\text{C}=\text{}$ ) and  $\delta(\text{CCl}_4)$ : 4.68—5.4 (8 H, m,  $4-\text{CH}=\text{CH}$ ,  $4-\text{C}=\text{CH}_2$ ), 2.62—2.82 (4 H, bm,  $=\text{C}-\text{CH}_2-\text{C}=\text{}$ ), and 2.0—2.23 (8 H, m,  $\text{CH}_2-\text{C}=\text{}$ ).

I.r. analysis of the final fraction obtained from the distillation showed it to be a rich mixture of conjugated and non-conjugated ketones (absorptions at 1715 and 1680  $\text{cm}^{-1}$ ). The ketones were separated by column chromatography. A pure sample of ketone, suggested by g.l.c. to be a 1:1 mixture of isomers, was obtained and identified by mass spectroscopy as a  $C_{15}$  cyclic ketone ( $M = 216$ ). I.r. analysis of the sample showed it to be a mixture of conjugated and non-conjugated ketones, while the n.m.r. spectrum, too complex to

<sup>7</sup> R. Baker, B. N. Blackett, and R. C. Cookson, *J.C.S. Chem. Comm.*, 1972, 802.

<sup>8</sup> R. Baker and A. H. Copeland, *Tetrahedron Letters*, 1976, 4535.

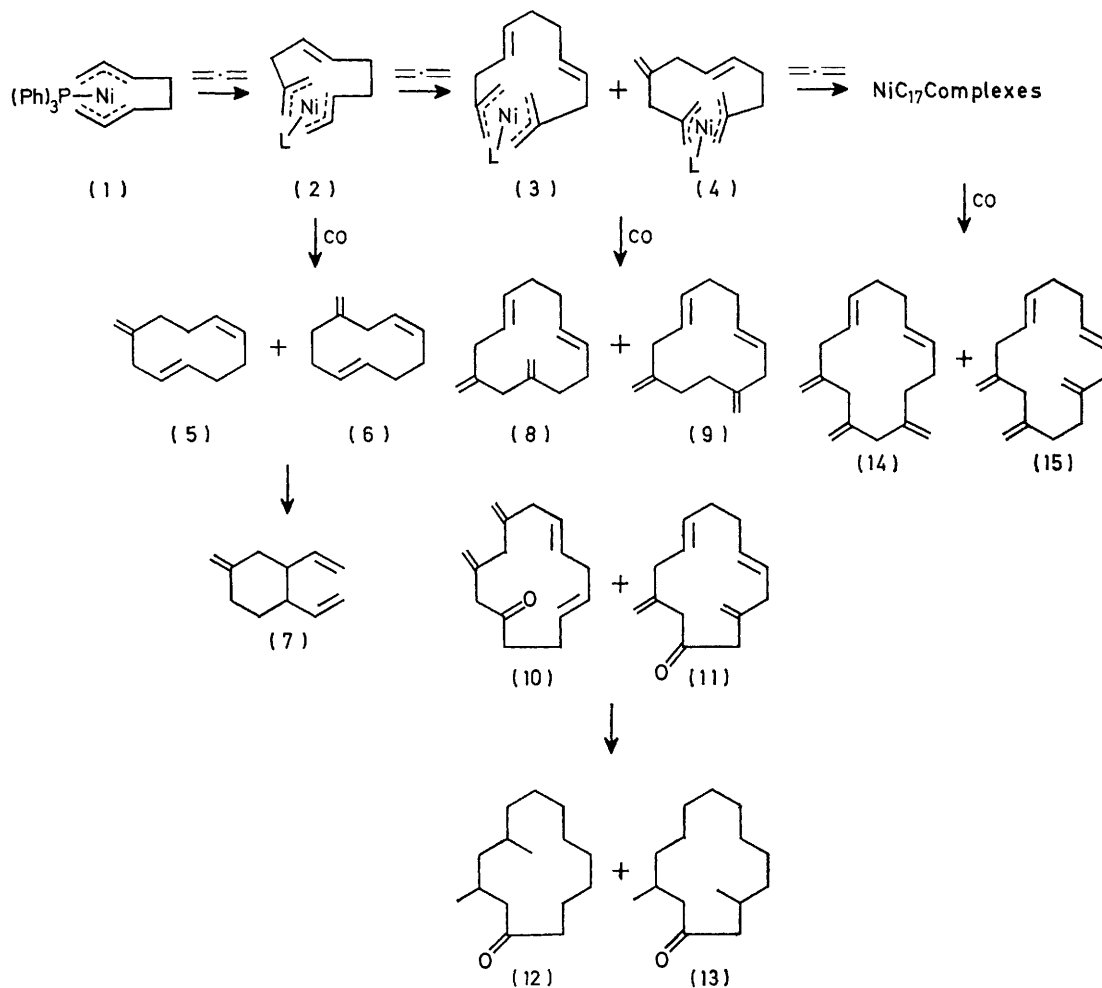
<sup>9</sup> P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel', Academic Press, New York, 1974, vol II, ch. 3.

<sup>10</sup> R. Baker and A. H. Copeland, *J.C.S. Perkin I*, 1977, 2497.

<sup>11</sup> 'Inorganic Synthesis', ed. G. W. Parshall, McGraw-Hill, New York, 1974, vol XV, p. 5.

assign, suggested the presence of at least three isomers. The  $C_{15}$  ketone mixture was hydrogenated (5% Pd-charcoal catalyst) and the saturated ketone isolated assigned to be a mixture of the isomeric structures (12) and (13) on the basis of the n.m.r. spectrum;  $\delta(CCl_4)$ : 0.96—2.63 (22 H, bs and bm, 4- $CH_2$ -C=O, 2 methine, 16- $CH_2$ ), 0.94 and 0.91 (6 H,  $2 \times d$ ,  $J_{CH_3-CH}$  6 Hz, CH- $CH_3$ ). In the two overlapping doublets observed, the signal centred at  $\delta$  0.94 was assigned as a methyl group  $\beta$  to the carbonyl group, while the doublet centred at

preparative g.l.c. without prior distillation. The new sample of  $C_{11}$  hydrocarbon isolated, when analysed, was apparently one product; however it was assigned to have the structures (5) and (6). Distinction between the structures could not be made from the n.m.r. spectrum;  $\delta(CCl_4)$ : 5.1—5.66 (4 H, m, CH=CH), 4.71 (2 H, bs, C= $CH_2$ ), 2.7 (2 H, bd,  $J_{CH-CH_2}$  7 Hz, =C- $CH_2$ -C=), 1.92—2.11 (8 H, m, - $CH_2$ -C=). I.r. analysis indicated the presence of both *cis*- and *trans*-double bonds (715 and 865  $cm^{-1}$ ) and also confirmed the absence of a



SCHEME

$\delta$  0.91 was assigned as a methyl group  $\delta$  to the carbonyl group. The observation of methyl groups in different environments indicates the presence of (12), while the presence of (13) was suggested by the greater intensity of the doublet at lower field.

In a second, similar reaction, the NiC<sub>8</sub> complex [from Ni(cod)<sub>2</sub>, 3.5 g, 12.6 mmol] was stirred with allene for 6½ h. G.l.c. analysis indicated that, in addition to those observed in the previous reaction, two further products of longer retention time had been formed. The C<sub>11</sub> hydrocarbon produced was also different from that obtained in the previous reaction and was isolated by

vinyl group. There was no evidence to suggest whether the C<sub>11</sub> hydrocarbon contained either or both these structures. The assignment made was based on a report on the co-oligomerisation reaction of butadiene with allene, in which both isomers were reported to be formed.<sup>12</sup> Further, both large-ring isomers of the C<sub>14</sub> hydrocarbons have been shown to be formed and there is no apparent reason why selective formation of only one C<sub>11</sub> isomer should occur.

The two new products formed were identified by mass

<sup>12</sup> P. Heimbach, H. Selbeck, and E. Troxler, *Angew. Chem. Internat. Edn.*, 1971, **10**, 659.

spectroscopy as two  $C_{17}$  hydrocarbons ( $M = 228$ ) and were assigned the structures (14) and (15). Only one of the samples was isolated pure;  $\delta(CCl_4)$ : 5.1—5.32 (4 H, m,  $CH=CH$ ), 4.62—4.92 (6 H, m,  $C=CH_2$ ), 2.64 (6 H, bs,  $=C-CH_2-C=$ ), and 2.0—2.36 (8 H, m,  $-CH_2-C=$ ). An assignment of the second structure was made by a comparison with the analogous  $C_{14}$  hydrocarbons which exhibited similar n.m.r. spectral patterns. With the exceptions of (5) and (6), all the hydrocarbons isolated from both the reactions were suggested to have a predominantly all-*trans* stereochemistry by the strong absorption at  $960\text{ cm}^{-1}$  and lack of absorption below  $850\text{ cm}^{-1}$  in their i.r. spectra.

The insertion of allene into the  $NiC_8$  complex (1) is suggested to proceed as in the Scheme. Formation of the new bis-allyl intermediate (2) can occur by the insertion of 1 mole equivalent of allene into (1). Treatment of (2) with carbon monoxide then favours coupling of the allyl groups and the large ring  $C_{11}$  hydrocarbons (5) and (6) can be formed. The thermal conversion of (5) and (6) to (7) can be expected *via* a Cope rearrangement and formation of (7) probably occurred during distillation of the product mixture. No attempt was made to determine the stereochemistry of the vinyl groups; however, the conversion of (5) and (6) into (7) has been reported to proceed stereospecifically *cis*.<sup>12</sup> No small-ring hydrocarbon derived from (2) was detected and a  $C_{12}$  ketone, the product of an insertion reaction, was detected in only trace quantities. Insertion of a second equivalent of allene into (2) can occur with the formation of the two new bis-allyl species (3) and (4). When (3) and (4) are treated with carbon monoxide, coupling of the allyl fragments is the favoured mode of reaction and the two large-ring hydrocarbons (8) and (9) can be formed. Small amounts of ketone insertion products are also formed and these were assigned the structures (10) and (11). Further insertion of allene into (3) and (4) can occur with formation of bis-allyl  $NiC_{17}$  complexes which on treatment with carbon monoxide, afford the large-ring hydrocarbons (14) and (15) from the coupling reaction.

Thus treatment of the  $NiC_{11}$ ,  $NiC_{14}$ , and  $NiC_{17}$  complexes, formed by the insertion of 1, 2, and 3 mole equivalents of allene into  $\alpha\omega$ -octadienediynickel (1), with carbon monoxide at  $-78^\circ\text{C}$ , favoured coupling of the allyl fragments to yield substituted  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$  cyclic hydrocarbons. A relatively small amount of a 13-membered ring ketone, derived from insertion of carbon monoxide into the  $NiC_{14}$  complex was also isolated. No smaller ring products, either hydrocarbon or ketone, were detected.

The present reactions, therefore, parallel those found in the successive insertion of allene into dodecatrienediynickel in which a series of  $NiC_{15}$ ,  $NiC_{18}$ ,  $NiC_{21}$ , and  $NiC_{24}$  bis- $\pi$ -allylnickel intermediates was formed.<sup>10</sup> Carbonylation of the  $NiC_{15}$  complex at  $-78^\circ\text{C}$  resulted in coupling of the allyl groups to yield 1-methylenecyclo-tetradeca-3,7,11-triene, whereas at  $0$ — $10^\circ\text{C}$  a 5 : 2 mixture of the  $C_{14}$  cyclic hydrocarbon and 1-methylene-

11-vinylcyclododeca-3,7-diene was produced. In addition, a small amount of a 15-membered ring ketone was produced.<sup>7</sup> Treatment of the  $NiC_{18}$  complexes, with carbon monoxide at both room temperature and at  $-78^\circ\text{C}$ , afforded exclusively 16-membered cyclic hydrocarbons. Similarly, carbonylation of the  $NiC_{21}$  complex gave exclusively 18-membered cyclic hydrocarbons. These results can be contrasted with carbonylation reactions of  $\alpha\omega$ -octadienediyl- and dodecatrienediynickel complexes. The former affords complete formation of hydrocarbon at  $-60^\circ\text{C}$ ,<sup>9</sup> whilst, under the same conditions, the latter yields a 2-vinylcycloundeca-5,9-dienone.<sup>13</sup>

*Selectivity of Addition of Allene to  $\alpha\omega$ -Octadienediynickel (1).*—Multiple insertion of allene has been shown to occur when the  $NiC_8$  complex (1) is treated with an excess of allene. Formation of a bis- $(\pi$ -allyl) $NiC_{15}$  complex derived from the insertion of 1 molar equivalent of allene into  $\alpha\omega$ -dodecatrienediynickel occurred selectively when the nickel complex was treated with a slight excess of allene at  $-10$  to  $20^\circ\text{C}$ . The  $NiC_8$  complex (1) was similarly treated with a limited quantity of allene in an attempt to achieve a more selective formation of the  $NiC_{11}$  complex (2).

Allene, from a gas burette, was passed into a solution of (1) [from  $Ni(\text{cod})_2$ , 3.1 g, 11.1 mmol] held at  $-28^\circ\text{C}$ . Uptake of the gas was stopped after  $1\frac{1}{2}$  mole equivalents (*ca.* 400 ml) had been absorbed, and the reaction mixture was left to stir at  $-28^\circ\text{C}$  for  $2\frac{1}{2}$  h before being warmed to room temperature and carbonylation overnight. G.l.c. analysis of the product mixture indicated the presence of  $C_{11}$  and  $C_{14}$  hydrocarbons in the ratio 1 : 1.6 and the overall yield of the reaction was estimated, by the use of an internal standard, to be *ca.* 20% based on  $Ni(\text{cod})_2$ .

This result suggests that selective formation of the  $NiC_{11}$  complex under these conditions is not a ready process. The product mixture formed was shown to contain a greater amount of  $C_{14}$  hydrocarbon, derived from the insertion of 2 mole equivalents of allene into (1), than the required  $C_{11}$  hydrocarbon suggesting that the  $NiC_{11}$  complex is susceptible to attack by allene. Thus, selective formation of the  $NiC_{11}$  complex appears unlikely.

In another experiment an excess of allene (10 ml, 150 mmol) was distilled into a solution of (1) [from  $Ni(\text{cod})_2$ , 3.5 g, 12.6 mmol] at  $-28^\circ\text{C}$  and stirred for various times before the mixture was cooled to  $-78^\circ\text{C}$  and carbonylated overnight. G.l.c. analysis enabled the relative amounts of the bis-allyl intermediates formed in the reactions to be estimated by a comparison of the peak areas of the products formed. The overall yield of the products, *i.e.* % conversion of the  $NiC_8$  complex based on  $Ni(\text{cod})_2$ , was estimated by the use of mesitylene as an internal standard added on termination of the reaction (Table). The results clearly show that insertion of 2 mole equivalents of allene into the  $NiC_8$  complex (1) is preferred. The product mixture formed after (1) had been stirred with allene for 1 h, contained consider-

<sup>13</sup> G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, 2, 105.

ably more  $C_{14}$  than  $C_{11}$  products. In addition, the formation of the  $NiC_{17}$  complexes, derived from the insertion of 3 mole equivalents of allene into (1), does not appear to be favoured. The concentrations of the  $C_{17}$  hydrocarbons detected in the product mixtures were too low

Addition of allene to  $\alpha\omega$ -octadienediynickel at  $-20^\circ C$

Time (h)	$C_{11}$	$C_{14}$	$C_{17}$	Conversion
1	1	1.85	trace	34%
2	1	2.16	trace	
5	1	1.97	0.26	58%
6½	1	1.87	0.33	

to be estimated in the shorter experiments and, after 5 h they represented only 8% of the product mixture. Similar experiments of the addition of allene to dodecatrienediynickel indicated a selective addition of 1 mole equivalent of allene could be obtained under controlled conditions<sup>6,7</sup> but, in the presence of an excess of allene, little selectivity was observed.<sup>10</sup>

**Reaction with Isocyanides.**—The addition of isocyanide to bis- $\pi$ -allylnickel complexes has, in general, been observed to afford higher yields of ketone insertion product, after hydrolysis, than the equivalent carbonylation reaction.<sup>6-9</sup> Notable exceptions are the reactions of  $\alpha\omega$ -dodecatrienediynickel, when a high yield of carbonyl insertion product was also isolated,<sup>13,14</sup> and the allene trimer nickel species (16) in which polymerisation of the product under the conditions of the hydrolysis has been suggested to occur.<sup>8</sup>

$\eta$ -Butyl isocyanide was added to a solution of the bis-allyl intermediates derived from the insertion of allene into the  $NiC_8$  complex (1) with the aim of isolating an increased yield of ketone insertion product. A solution of the  $NiC_8$  + allene intermediates was prepared by distilling an excess of allene (20 ml, 300 mmol) into a solution of (1), stirring for 5 h at  $-28^\circ C$ , cooling to  $-78^\circ C$ , and adding *n*-butyl isocyanide (12 ml, 150 mmol). The clear, dark red solution was allowed to warm slowly overnight. The product mixture was hydrolysed with dilute acid and stirred with activated charcoal to remove the dark red nickel complexes. I.r.

isolated by preparative g.l.c. and assigned the structure (17) on the basis of the n.m.r. spectrum:  $\delta(CCl_4)$  5.20—4.76 (6 H, m,  $CH=CH$ ), 3.04—2.87 (4 H, m,  $=C-CH_2-C=O$ ), 2.69 (2 H, bd,  $J_{CH-CH_2}$  6 Hz,  $=C-CH_2-C=$ ), and 2.08—2.02 (4 H, m,  $-CH_2-C=$ ). A sample of  $C_{15}$  ketone was also isolated by preparative g.l.c. and shown by n.m.r. to be a mixture of conjugated and non-conjugated isomers similar to that isolated in the carbon monoxide insertion reaction. The absence of absorptions at 990 and 910  $cm^{-1}$  in the i.r. spectrum confirmed the absence of a vinyl group and suggested that again only the large-ring ketones (10) and (11) were formed. The other ketone products were (18) and (19) derived directly from (1) and have previously been reported.<sup>8</sup>

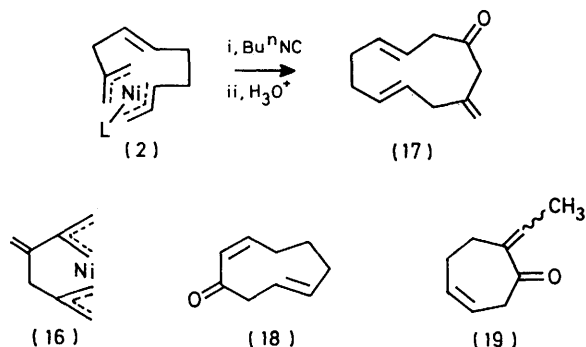
G.l.c. analysis of the combined ketone fractions showed the ratios of products to be (18):(19):17):(10)+(11) = 1:0.31:0.32:0.71. Thus, the yield of (17) could be estimated at 4% and the yield of (10)+(11) at 6%. A comparison between the g.l.c. traces of the product mixture and the combined ketone fractions enabled the ratio of coupled:insertion products for the  $NiC_{11}$  complex (2) to be estimated at 3.3:1 and for the  $NiC_{14}$  complexes (3) and (4) at 4.5:1.

Thus insertion of *n*-butyl isocyanide is not markedly more effective than insertion of carbon monoxide into bis- $\pi$ -allylnickel intermediates derived from reaction of allene with  $\alpha\omega$ -octadienediynickel (1). This is in contrast to other examples where higher yields of ketone can be obtained by isocyanide insertion, followed by hydrolysis, compared to carbonylation. A mixture of cyclic ketones was obtained in *ca.* 40% yield on reaction of  $\alpha\omega$ -octadienediynickel with *n*-butyl isocyanide followed by hydrolysis<sup>8</sup> but hydrocarbon products were formed on carbonylation.<sup>9</sup> Insertion of isocyanides to the  $NiC_{15}$  and  $NiC_{18}$  complexes obtained by addition of allene to  $\alpha\omega$ -dodecatrienediynickel resulted in higher yields of ketone than from the carbonylation reaction.<sup>10</sup>

#### EXPERIMENTAL

The preparation of the general reagents has been described.<sup>10</sup> Unless otherwise stated, all g.l.c. analyses were performed on a 3 m, 15% Carbowax 20M column with a programmed temperature rise of 100—200  $^\circ C$  at 16  $^\circ C$   $min^{-1}$ .

**Preparation of the  $\alpha\omega$ -Octadienediynickel Complex (1).**—Dry ether (20 ml) was placed in a 100 ml three-necked flask equipped with a pressure-equalising dropping funnel and a Drikold-acetone condenser, and the apparatus evacuated and flushed with argon at least three times.  $Ni(cod)_2$ <sup>11</sup> (3.87 g, 14.1 mmol) was weighed into the flask and the ethereal suspension cooled to  $-25^\circ C$ . A solution of triphenylphosphine in diethyl ether (3.67 g, 13.9 mmol in *ca.* 25 ml) was prepared, purged with argon and added, *via* the dropping funnel, to the suspension of  $Ni(cod)_2$ . A thick orange suspension formed. Excess of butadiene (30 ml) was distilled into the reaction mixture at  $-25^\circ C$ ; the orange suspension rapidly dissolved to give a dark red



analysis of the mixture indicated the presence of carbonyl compounds. The ketones were separated by column chromatography (0.94 g) and a sample of  $C_{12}$  ketone was

<sup>14</sup> H. Breil and G. Wilke, *Angew. Chem. Internat. Edn.*, 1970, **9**, 367.

solution. Excess of butadiene was removed under reduced pressure (15 mmHg) at  $-25^{\circ}\text{C}$  and the inert atmosphere readmitted. This solution of the  $\text{NiC}_8$  complex (1) was used as the starting point for all reactions.

*Reaction of (1) with an Excess of Allene for 2 Hours.*—An ethereal solution of the  $\text{NiC}_8$  complex (1) was prepared [from  $\text{Ni}(\text{cod})_2$  (7 g, 27 mmol)] and cooled to  $-25^{\circ}\text{C}$ . Dried allene (12 ml, 180 mmol) was distilled into the solution and the mixture stirred at  $-25^{\circ}\text{C}$  for 2 h before being cooled to  $-78^{\circ}\text{C}$  and passage of carbon monoxide. Carbonylation took place for 16 h during which period the mixture was allowed to warm slowly to room temperature, and the dark red colour of the solution faded. The pale orange solution formed was extracted into light petroleum (b.p.  $30-40^{\circ}\text{C}$ ): A large amount of orange precipitate appeared; this was filtered off and the solvent was evaporated from the filtrate. The product mixture was fractionally distilled to give a mixture of cyclo-octa-1,5-diene and 4-vinylcyclohexene ( $<50^{\circ}\text{C}/15$  mmHg, 6.2 g), mainly (7) ( $25^{\circ}\text{C}/1$  mmHg, 0.72 g),<sup>12</sup> a mixture of (7), (8), and (9) ( $63^{\circ}\text{C}/1$  mmHg, 0.68 g), a mixture of (8) and (9) ( $120^{\circ}\text{C}/1$  mmHg, 1.02 g), and a mixture of (10) and (11) ( $<200^{\circ}\text{C}/1$  mmHg, 1.53 g). [Found: C, 88.75; H, 10.55. (8) and (9),  $\text{C}_{14}\text{H}_{20}$ , require C, 89.3; H, 10.75%,  $m/e$  188(16%),  $M$ , 173(22), 145(36), 131(36), 119(38), 105(53), 93(62), 91(100), and 79(87);  $\nu_{\text{max}}$  3 070, 3 010, 2 980, 2 910, 2 850, 1 640, 1 435, 960, and  $890\text{ cm}^{-1}$ . Definitive assignment could not be made to (8) or (9) but spectra were also obtained for the other isomer,  $m/e$  188(11%),  $M$ , 173(18), 145(32), 131(38), 119(39), 105(58), 93(58), 91(100), and 79(79);  $\nu_{\text{max}}$  3 070, 3 010, 2 980, 2 910, 2 845, 1 640, 1 435, 968, and  $890\text{ cm}^{-1}$ .

*Hydrogenation of Compounds (10) and (11).*—The ketone distilled fraction was further purified by column chromatography (0.54 g) and 41 mg hydrogenated over 5% Pd-charcoal catalyst (20 mg). A total of 181 ml was absorbed at room temperature which corresponds to 4 molar equivalents. The solution was filtered through Kieselguhr to remove the catalyst and the solvent evaporated to afford a colourless oil containing (12) and (13) (38 mg, 90%) (Found:  $M$ , 224.213 6.  $\text{C}_{15}\text{H}_{28}\text{O}$  requires  $M$ , 224.214 0)  $m/e$  224(6%),  $M$ , 209(3), 166(4), 111(17), 95(11), 85(40), 69(34), 55 (75), and 41(100);  $\nu_{\text{max}}$  2 950, 2 920, 2 860, 1 710, and  $1 460\text{ cm}^{-1}$ .

*Reaction of (1) with an Excess of Allene for 6.5 Hours.*—A solution of the  $\text{NiC}_8$  complex (1) [from  $\text{Ni}(\text{cod})_2$  3.3 g, 21 mmol] was prepared and stirred with allene (10 ml, 150 mmol) for 6.5 h at  $-25^{\circ}\text{C}$ . The dark red solution was cooled to  $-60^{\circ}\text{C}$  and carbon monoxide was passed through it while the solution was warmed to room temperature over 16 h. G.l.c. analysis of the orange crude product mixture indicated that, in addition to those observed in the previous reaction, two further products of longer retention time had been formed. A comparison of the g.l.c. trace of the product mixture with that of the hydrocarbon fractions isolated after chromatography enabled the ratio of coupled:insertion products for the  $\text{NiC}_{14}$  complexes to be estimated at 5:1. A similar estimate for the  $\text{NiC}_{11}$  complex could not be obtained since the  $\text{C}_{12}$  ketone was formed in only trace amounts. A second sample of  $\text{C}_{11}$  hydrocarbon was isolated by preparative g.l.c. and identified to be a mixture of (5) and (6).<sup>10</sup> The two new products observed were detected by g.l.c. to be in the hydrocarbon fractions and samples of each were isolated by preparative g.l.c. and identified to be the adducts (14) and (15) derived by addition of 3 mole equivalents of allene to (1) [Found: C, 88.45; H, 10.35. (14) and (15),  $\text{C}_{17}\text{H}_{24}$  require C, 89.4; H, 10.6%]. The two

isomers had the following spectral properties,  $m/e$ , 228(10%,  $M$ ), 213(10), 173(18), 145(33), 133(43), 117(35), 105(83), 91(100), and 79(90);  $\nu_{\text{max}}$  3 070, 2 980, 2 910, 2 850, 1 460, 1 435, 970, and 895;  $m/e$  228(4%,  $M$ ), 213(12), 173(17), 145(26), 131(30), 119(35), 105(100), 91(80), and 79(65);  $\nu_{\text{max}}$  3 070, 3 010, 2 980, 2 910, 2 850, 1 460, 1 435, 970, and  $895\text{ cm}^{-1}$ .

*Reaction of (1) with 1.5 mole Equivalents of Allene.*—A solution of the  $\text{NiC}_8$  complex was prepared [from  $\text{Ni}(\text{cod})_2$  3.05 g, 11.1 mmol] and allene, from a gas burette, was passed into it in a sealed system; uptake of the gas occurred. The inlet tube was best positioned just above the surface of the solution and the system was initially flushed with allene to remove any blanket of argon. Uptake of the gas was stopped after 1.5 mole equivalents (ca. 400 ml) had been absorbed and the mixture was left to stir at  $-25^{\circ}\text{C}$ , under argon, for 2.5 h. The dark red solution was then warmed to room temperature and carbonylated until the colour of the solution had faded and a small quantity of orange precipitate appeared. G.l.c. analysis of the crude product mixture indicated the presence of  $\text{C}_{11}$  and  $\text{C}_{14}$  hydrocarbons in the ratio (5) and (6):(8) and (9) = 1:1.6. Mesitylene (0.194 g) was added to the product mixture, and a comparison of peak areas of the internal standard with those of the hydrocarbon products enabled the yield of the reaction to be estimated at 20% based on  $\text{Ni}(\text{cod})_2$ .

*Reaction of (1) with an Excess of Allene.*—Excess of allene (10 ml, 150 mmol) was distilled into a solution of the  $\text{NiC}_8$  complex (1) [from  $\text{Ni}(\text{cod})_2$  3.5 g, 12.6 mmol] at  $-28^{\circ}\text{C}$  and stirred for 5 h before the mixture was cooled to  $-78^{\circ}\text{C}$  and carbonylated overnight. G.l.c. analysis enabled the relative amounts of the bis-allyl intermediates formed in the reactions to be estimated by a comparison of the peak areas of the products formed. The overall yield of the products, i.e. % conversion of the  $\text{NiC}_8$  complex based on  $\text{Ni}(\text{cod})_2$ , was estimated by the use of mesitylene as an internal standard added on termination of the reaction (Table).

*Reaction of the  $\text{NiC}_8$  + Allene Complexes with *n*-Butyl Isocyanide.*—Dried allene (20 ml, 300 mmol) was distilled into an ethereal solution of the  $\text{NiC}_8$  complex (1) [from  $\text{Ni}(\text{cod})_2$  6.8 g, 24.7 mmol] and the mixture left to stir at  $-28^{\circ}\text{C}$  for 5 h. The dark red solution was cooled to  $-78^{\circ}\text{C}$  and *n*-butyl isocyanide (12 ml, 150 mmol) in ether (20 ml) was added dropwise. The mixture was left to stir at  $-78^{\circ}\text{C}$  for 4 h before being allowed to warm slowly to room temperature. The orange solution formed was then cooled to  $0^{\circ}\text{C}$  and hydrolysed by a dropwise addition of 10 ml of a 30% solution of glacial acetic and concentrated sulphuric acids (9:1, v/v). The solution immediately turned dark red and the mixture was left to stir at  $0^{\circ}\text{C}$  for 1.5 h. The organic layer was separated and the aqueous phase extracted with  $3 \times 50$  ml portions of ether. The combined organic extracts were washed with saturated sodium hydrogen carbonate solution and distilled water, and dried ( $\text{MgSO}_4$ ). The ether solution was filtered and stirred with  $4 \times 10$  g portions of activated charcoal to remove the dark red nickel complexes and the solvent evaporated from the resultant pale yellow solution. G.l.c. analysis of the product mixture suggested that very little isocyanide insertion into the  $\text{NiC}_8$  + allene complexes had taken place, although the  $\text{C}_9$  ketones (18) and (19) were very much in evidence. The ketones were separated by column chromatography (0.94 g). G.l.c. analysis of the combined ketone fractions showed the ratio of products to be (18):(19):(17):(10)+(11) = 1:0.31:0.32:0.71. Thus the yield of  $\text{C}_{12}$  ketone (17)

could be estimated at 4% and the yield of C<sub>15</sub> ketones (10) and (11) could be estimated at 6%. A comparison between the g.l.c. traces of the product mixture and the combined ketone fractions, enabled the ratio of coupled:insertion products for the NiC<sub>11</sub> complex (2) to be estimated at 3.3:1 and for the NiC<sub>14</sub> complexes (3) and (4) at 4.5:1. A sample of C<sub>12</sub> ketone was isolated by preparative g.l.c. and assigned the structure (17), *m/e* 176(9%, *M*), 161(2),

148(3), 135(7), 122(17), 93(28), 91(19), 79(100);  $\nu_{\max}$ . 3 070, 3 010, 2 910, 1 710, 1 640, 970, and 895 cm<sup>-1</sup>.

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