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## Reaction of Dodecatrienylnickel with Allene; Formation of Muscone

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Summary The dodecatrienylnickel complex (1) absorbs 1 mol. equiv. of allene to yield the new bis- $\pi$ -allyl intermediate (2); this absorbs a second mol. equiv. of allene to give eventually two isomeric dimethylene-cyclohexadecatrienes (4) and (5), or carbon monoxide to give the cyclic hydrocarbons (6) and (7) accompanied by the unsaturated ketone (8), which on hydrogenation forms ( $\pm$ )-muscone.

The dodecatrienylnickel complex (1) readily yields cyclododecatriene<sup>1</sup> and its reaction with carbon monoxide and isocyanides has been reported to give 11- and 13-membered ring ketones<sup>2</sup> and imines,<sup>3</sup> respectively. We now report the reaction of (1) with allene which, under various conditions, leads to a variety of compounds with larger rings including (8) (albeit in low yield), which on hydrogenation yields  $(\pm)$ -muscone.<sup>4</sup>

When an excess of allene is distilled into a solution of (1) (prepared from butadiene and bis-cyclo-octadienenickel)<sup>†</sup> at  $-50^{\circ}$  in ether, and the mixture is allowed to warm slowly to  $20^{\circ}$  and then stirred with aqueous KCN, a mixture of hydrocarbons is obtained consisting of cyclododecatrienes (30%) and a 4:1 mixture of 1,14- and 1,15-bis-methylene-cyclohexadeca-3,7,11-triene (4) and (5) (15%) together with 1,2,4,6,9-pentamethylenecyclodecane (3) (45%). (3) is known to be formed by the cyclo-oligomerisation of allene in the presence of bis-cyclo-octadienenickel<sup>5</sup> and was not observed in subsequent experiments when care was taken to remove this before addition of allene.

When allene from a gas reservoir was allowed to react with an ether solution of (1) at -20 to  $-10^{\circ}$  the initially rapid uptake decreased and ceased after 2 h. Cooling to  $-70^{\circ}$  and passing in carbon monoxide overnight and then warming slowly to  $20^{\circ}$ , yielded, after decomposition with aqueous KCN, hydrocarbons consisting mainly of a 2:1 mixture of cyclododecatrienes and 1-methylenecyclotetradeca-3,7,11-triene (6).

However, when the above reaction was carried out by passing in carbon monoxide at  $0-10^{\circ}$  and the products were chromatographed on silica, on elution with light petroleum, cyclododecatrienes, followed by a 5:2 mixture of (6) and 1-methylene-11-vinylcyclododeca-3,7-diene (7) were obtained and the latter was separated by preparative g.l.c. Further elution with light petroleum-ether (15:1) gave fractions containing a carbonyl compound (8),  $\nu_{max}$  1713 cm<sup>-1</sup>, which on hydrogenation gave an oil with a strong musk odour,  $\nu_{max}$  1720 cm<sup>-1</sup>. This was proved to be identical with authentic ( $\pm$ )-muscone.<sup>‡</sup> Excluding cyclododecatrienes, (8) represented *ca.* 4-5% of the total product.

The reactions are considered to proceed through the bis- $\pi$ -allyl intermediate (2) formed by addition of one mol. equiv. of allene to (1). (2) is best prepared when allene gas is allowed on to the surface of the solution of (1) so that the

allene concentration is never high. Carbonylation of (2) then either promotes ring closure to give the cyclic hydrocarbons or carbonyl insertion occurs to yield the muscone



Reagents: i, excess of allene,  $-50^{\circ}$ ; ii,  $20^{\circ}$ , biscyclo-octadienylnickel present; iii, slight excess of allene,  $-20^{\circ}$  to  $-10^{\circ}$  in ether; iv, excess of allene,  $20^{\circ}$ ; v, CO,  $0-10^{\circ}$  in ether; vi, CO,  $-70^{\circ}$ ; vii,  $20^{\circ}$ , several hours; viii,  $[H_2]$ .

- † Unchanged bis-cyclo-octadienenickel was not removed in this experiment.
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precursor (8). By addition of further allene to (2) insertion of a second mol. equiv. occurs and the hydrocarbons (4) and (5) are formed, probably through the bis- $\pi$ -allyl intermediates (10) and (11). Unlike (1), spontaneous decomposition of (2) (20 h at 20°) results in a 1,11-hydride shift to give the linear pentaene (9).

Reaction of (2) with CO favours coupling of the  $\pi$ -allyl groups similar to that observed for bis- $\pi$ -allylnickel<sup>6</sup> and the complexes  $(12)^7$  and  $(13)^8$  but in marked contrast to (1) in which insertion is favoured to give 11- and 13-membered ring ketones (ca. 10:1) in high yield.<sup>2</sup> Furthermore, the insertion of CO into (2) leads to the formation of the 15rather than the 13-membered ring adduct (by at least 15:1).

We are unable to assign the stereochemistry of all the products with certainty, but the predominance of the alltrans-form, in each case, is indicated by the lack of absorption due to cis-double bonds in the i.r. spectra. All other physical data are fully consistent with the structures assigned.

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