Reaction of Dodecatrienylnickel with Allene; Formation of Muscone

By R. Baker,* B. N. Blackett, and R. C. Cookson*
(*Department of Chemistry, The University, Southampton* SO9 5NH)

Summary The dodecatrienylnickel complex (**1**) absorbs 1 mol. equiv. of allene to yield the new bis-π-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 (±)-muscone.

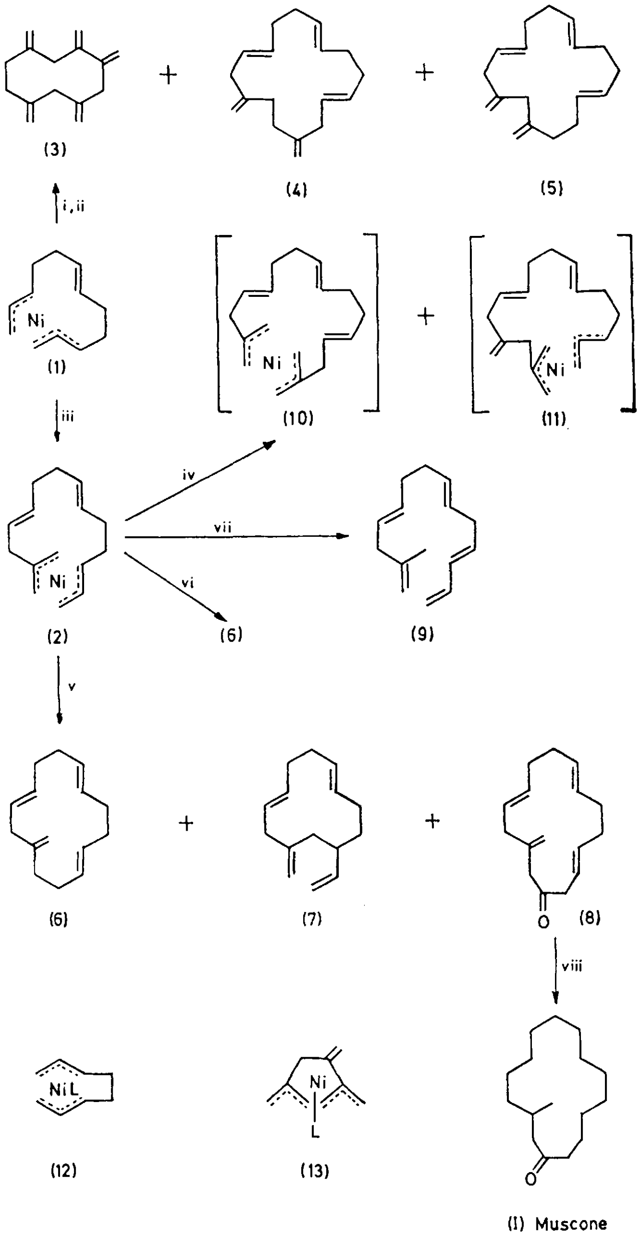
The dodecatrienylnickel complex (**1**) readily yields cyclododecatriene[1] and its reaction with carbon monoxide and isocyanides has been reported to give 11- and 13-membered ring ketones[2] and imines,[3] respectively. We now report the reaction of (**1**) with allene which, under various conditions,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

When an excess of allene is distilled into a solution of (**1**) (prepared from butadiene and bis-cyclo-octadienenickel)† at −50° in ether, and the mixture is allowed to warm slowly to 20° 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-methylenecyclohexadeca-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[5] 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° the initially rapid uptake decreased and ceased after 2 h. Cooling to −70° and passing in carbon monoxide overnight and then warming slowly to 20°, 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° 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**), ν_{max} 1713 cm^{-1}, which on hydrogenation gave an oil with a strong musk odour, ν_{max} 1720 cm^{-1}. This was proved to be identical with authentic (±)-muscone.‡ Excluding cyclododecatrienes, (**8**) represented *ca.* 4—5% of the total product.

The reactions are considered to proceed through the bis-π-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°; ii, 20°, biscyclo-octadienylnickel present; iii, slight excess of allene, −20° to −10° in ether; iv, excess of allene, 20°; v, CO, 0—10° in ether; vi, CO, —70°; vii, 20°, several hours; viii, [H_2].

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† Unchanged bis-cyclo-octadienenickel was not removed in this experiment.

‡ Kindly provided by Dr. G. Ohloff, Firmenich & Cie, Geneva.

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-π-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 π-allyl groups similar to that observed for bis-π-allylnickel[6] 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.[2] Furthermore, the insertion of CO into (**2**) leads to the formation of the 15- rather 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 all-*trans*-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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