Regiospecificity in the Reactions of Bis-π-allylnickel Intermediates with Nucleophilic and Electrophilic Reagents

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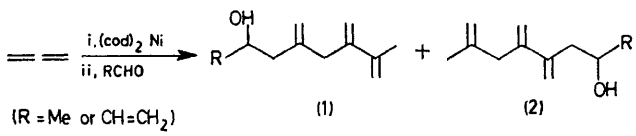
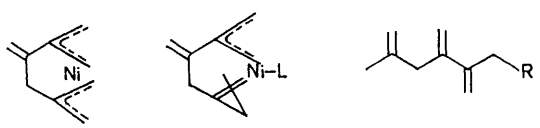
Summary Reactions of the bis-π-allylnickel complexes derived from isoprene and allene with active methylene compounds, amines, and aldehydes have indicated a selectivity which has been related to the σ-π character of the structure of the complexes.

A RANGE of reactions of bis-π-allylmetal derivatives obtained from butadiene, isoprene, and allene have been studied.[1] We report that considerable regiospecificity has been observed in the reaction of unsymmetrical bis-π-allylnickel complexes, derived from isoprene and allene.

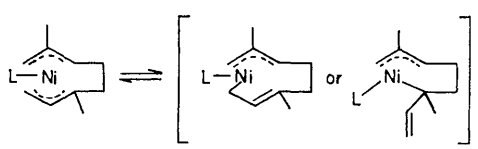


(R = Me or $CH{=}CH_2$) (1) (2)



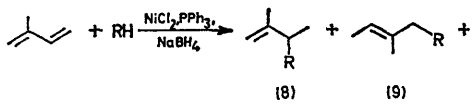
(3) (4) (5)

(R = NR'_2 or CHX_2 where X = CO_2Et *etc.*)

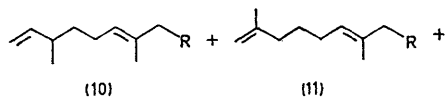


(6) (7)

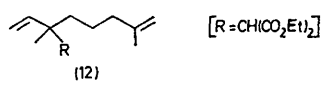
Addition of allene (0·07—0·1 mol) to bis(cyclo-octadiene)-nickel(0) [$(cod)_2Ni$], prepared from nickel acetylacetonate (0·02 mol)[2] in ether, gave a red solution containing the bis-π-allylnickel complex (**3**).[3] Acetaldehyde (0·025 mol) was then added at −78 °C and the solution allowed to warm slowly to room temperature. Alternatively, a solution of (**3**) was first treated with an organophosphorous compound (0·02 mol) at −30 °C followed by the addition of the aldehyde. Two isomeric alcohols (**1**) and (**2**) were obtained in a ratio of *ca.* 7 : 1.† The highest yields were obtained in the presence of the co-ordinating ligands PPh_3 (33%) and P(cyclohexyl)$_3$ (29%) and on addition of dimethylformamide (32%).‡ Similar reactions occurred with acrolein and a comparable selective phenomenon was observed.



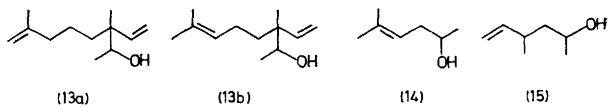
(8) (9)



(10) (11)



(12)



(13a) (13b) (14) (15)

In contrast to the predominant formation of (**1**) from reaction of the aldehydes with (**3**), reaction with amines and active methylene compounds gave high selectivity to forma-

† All assigned structures are fully consistent with spectroscopic data.

‡ Yields based on $Ni(acac)_2$.

tion of the adducts (**5**).[4] *X*-Ray and n.m.r. studies have already shown that, in the presence of certain ligands, the structure of (**3**) is more closely represented as a σ-π-allylnickel species (**4**).[5] From the present results, it appears that reaction of the aldehyde occurs preferentially at the σ-allylnickel bond and amines and active methylene compounds react at the π-allyl sites.

Reactions with isoprene point to a similar situation on treatment with the complex (**6**). In the presence of $NiCl_2$ (3·3 mmol), PPh_3 (6·6 mmol), and $NaBH_4$ (13·3 mmol) in ethanol, isoprene (0·13 mol) and diethyl malonate (0·043 mol gave, after 24 h at 20 °C, a 64% conversion into a mixture containing (**8**) (14%), (**9**) (17%), (**10**) (39%), (**11**) (10%), and (**12**) (15%). Again, physical data indicate that, in the presence of ligands, the bis-π-allylic complex (**6**) displays the σ-π-structure (**7**).[6] Whilst some 1 : 1 adducts, and a product derived from tail–tail isoprene dimerisation, are also obtained, the predominant adduct is formed by reaction of the nucleophilic reagent at the π-allyl site of (**7**).

A solution of isoprene (200 mmol) and cyclododecatriene–triphenylphosphinenickel,[7] derived from nickel acetylacetonate (19·4 mmol), in ether, was stirred overnight at 0 °C, cooled to −30 °C, and acetaldehyde (88 mmol) was added. The solution was stirred for a further 6 h whilst allowing it to warm to room temperature. Addition of saturated aqueous NaCN and extraction with ether gave both 2 : 1 (40%) and 1 : 1 (18%) isoprene–aldehyde adducts.‡ The former consisted of mainly (**13**) (>90%, **13a** : **13b**, 1 : 1) and the major product of the latter was (**14**) (65%) together with (**15**) (35%). The reaction of aldehyde, therefore, indicates a preference for attack at the σ-allyl group of (**7**).

It is clear that the predominant products from reaction of amines and active methylene compounds with (**4**) and (**7**) are derived by attack at the π-allyl site whilst aldehydes undergo preferential reaction at the σ-allyl group of the nickel complexes. The specificity observed in the present reactions might be generally applicable to other nucleophilic and electrophilic reagents. Further studies will indicate if the selectivity is related to the reactivity of the electrophile and the electronic properties of the organophosphorous ligands.

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