Reaction of the π-Allyl Groups of the Dodecatrienylnickel Complex with Aldehydes, Acetyl Chloride, and Allyl Bromide

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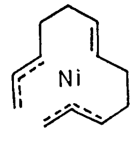
Summary Acetaldehyde, acetyl chloride, and acrolein add to one of the π-allyl groups of dodecatrienylnickel (**1**) giving long chain organic compounds; in the presence of allyl bromide, addition to both π-allyl groups occurs giving products of increased chain length.

Corey and his co-workers have demonstrated that the reactions of π-allylnickel bromides with halides, aldehydes, ketones, or epoxides can be valuable in organic syntheses.[1]



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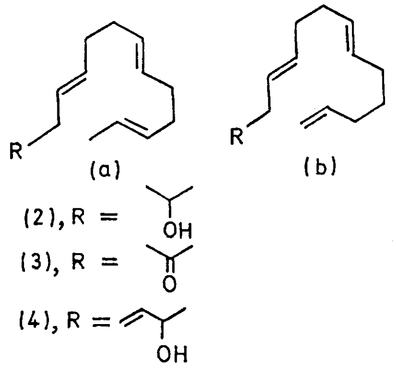

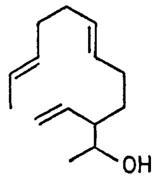

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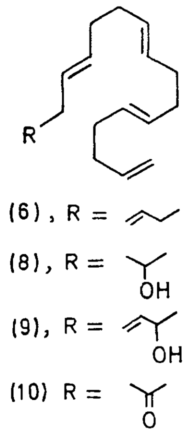

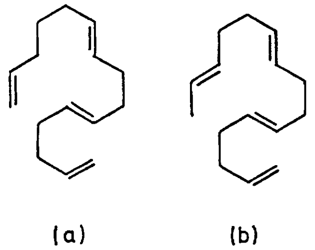

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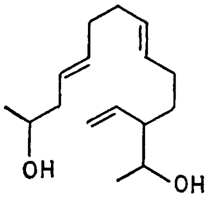
Similarly, Wilke has demonstrated the extensive chemistry associated with 1,3-dienes and Ni⁰ complexes.[2] Here we report the reaction of (**1**) with acetaldehyde, acetyl chloride and allyl bromide.

A typical experiment involved the addition of an ethereal solution of the reagent to (**1**) dissolved in ether at −78°. The solution was allowed to reach room temperature and stirring was continued for 4—6 h; the products were extracted after addition of an aqueous solution of potassium cyanide. From acetaldehyde, a 30—40% conversion into a mixture of (**2**) [66% consisting of a 2:1 ratio of (**2a**) : (**2b**)], (**5**) (5%), and a mixture of diols (22%) was obtained together with a small amount of cyclododeca-1,5,9-triene.† Similarly, (**3**) [consisting of a 1:3 mixture of (**3a**) : (**3b**)] and (**4**) were obtained in *ca.* 35% yield from reaction with acetyl chloride and acrolein, respectively. Some C_{18}-diol was formed in the latter reaction by addition of 2 moles of acrolein. A 5:2 mixture of (**6**) : (**7**) was obtained from the addition of allyl bromide (2 mol) to (**1**) in about 40% yield. On the basis of its n.m.r. spectrum, (**7**) was shown to be a 3:2 mixture of (**7a**) and (**7b**). 3,3-Dimethylallyl bromide, benzyl bromide, and methoxymethyl chloride reacted to give analogous products. Small amounts of cyclododeca-1,5,9-triene, divinylcyclododecadiene, and cyclohexadecatetraene were also obtained in these reactions; the latter has been previously reported in the reaction of butadiene and nickel complexes.[3]



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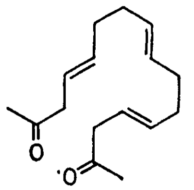

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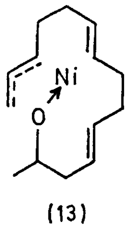

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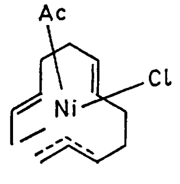

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Addition of a second mole of acetaldehyde or acetyl chloride yielding (**11**) and (**12**) is facilitated in the presence of aqueous cyanide or other activating ligands.‡ Compounds (8)—(**10**) are obtained by reaction of (**1**) with acetaldehyde, acrolein, or acetyl chloride together with, or followed by, allyl bromide.

Compounds (**13**) and (**14**) are likely intermediates in the reaction of (**1**) with aldehyde and acetyl chloride, respec-

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

‡ Use of CO also results in the formation of small amounts of other ketonic products from CO insertion. Oxygen is an effective ligand but its use results in hydroxyl insertion into the remaining π-allyl groups of (**1**) and (**13**).

tively. Hydrolysis of the intermediates (**1**), (**13**), and (**14**) is facilitated by the addition of strong ligands† such as CO or CN^-. The observations are consistent with a mechanism involving co-ordination of the cyanide ion to the Ni atom of intermediates (**1**) and (**13**) and conversion into σ-allyl intermediates with consequent enhancement of reactivity towards electrophilic reagents.

π-Allylnickel bromides react readily with a variety of alkyl halides,[1] whereas (**1**) requires an activated halide, *e.g.* allyl or benzyl halides. The difference in reactivity between functional groups is of importance in the simultaneous addition of two different groups to the π-allyl groups of (**1**). Sequential addition to (**1**) is facilitated by the fact that the intermediates (**13**) and (**14**), formed by reaction of one of the π-allyl groups, react readily with allyl bromide but require the assistance of a strongly co-ordinating ligand to react further with aldehyde or acetyl chloride. (**13**) and (**14**) have distinctly different reactivities from (**1**) itself. Hence a group of reagents will not necessarily display the same order of reactivity towards the second π-allyl group of (**1**) as to the first. This fact promises to be of value in designing methods for the specific synthesis of a wide variety of nonsymmetrical long chain compounds.

We acknowledge financial support from the S.R.C.

(*Received*, 22*nd December* 1971; *Com.* 2174.)

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[1] E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, 1967, **89**, 2755; E. J. Corey and E. K. W. Wat, *ibid.*, p. 2757.

[2] P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1969, **8**, 29; G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanada, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151; G. Wilke, *ibid.*, 1963, **2**, 105.

[3] H. W. B. Reed, *J. Chem. Soc.*, 1954, 1931.