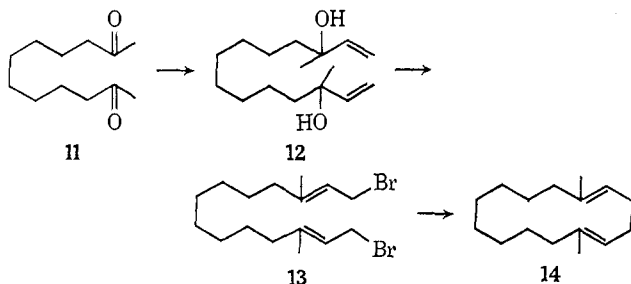


acetate **7c** with acetic anhydride in pyridine. The tetrahydropyranyl ethers were selectively removed by heating in 95% ethanol containing a trace of *p*-toluenesulfonic acid;¹⁸ the overall yield from **7a** was 90%. The resulting diol **9a** upon treatment with phosphorus tribromide yielded **9b** which upon reaction with nickel tetracarbonyl in *N*-methylpyrrolidone under standard conditions⁸ gave a 25% yield of monomeric products shown to be a mixture of isomeric trienes **10a**.

The mixture of acetates **10a** was treated with LAH followed by Jones oxidation to give in 50% yield enones **10c**. This material upon reaction with methyl lithium gave a mixture of alcohols **10d** which were chromatographically identical with and spectrally similar to natural isocembrol (isolated from *Pinus albicaulis*). The mixed alcohols were treated with a trace of *p*-toluenesulfonic acid in benzene to give a mixture of hydrocarbons which, although a single spot on tlc, proved to be a mixture of two major and several minor components upon vpc analysis. Of the two major components, the more rapidly moving one (35% of mixture) had an identical retention time as cembrene on coinjection. This material was separated from the other components of the mixture by preparative tlc on silver nitrate impregnated plates to give crystalline cembrene which was spectrally identical with authentic material and which upon recrystallization has mp 57–59°, undepressed upon admixture with an authentic sample.

During the course of this investigation, a variety of related synthetic steps was studied, and the following two observations are worthy of mention. When direct coupling of keto dibromide **8b**, prepared from **7a** by hydrolysis to diol **8a**¹⁸ and by conversion to dibromide **8b** using mesyl bromide and lithium bromide,¹⁹ was attempted, there was obtained a complex mixture of products, in which the enone functionality had disappeared. Apparently, the initially formed π -allyl nickel bromide added to the conjugate system followed by further reaction; similar conjugative additions are known.²⁰ Masking the carbonyl group as a methoxyimine derivative did not change the reaction course.

The poor yield on the nickel tetracarbonyl coupling reaction was disappointing and reasons for the low yield were evaluated. It has been reported earlier²¹ that the substitution of methyl groups on both allylic double bonds decreased the yield of 12-membered ring



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1,5-diene from **59** to 4%. With the 14-membered ring dibromide **13**, prepared from sebacic acid *via* diketone **11** and diallyl alcohol **12**, it was found that the ring formed in 70% yield, an identical result as reported for the unsubstituted case.⁸ This result would indicate in this ring size the other double bond played an important role.

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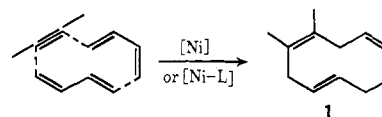
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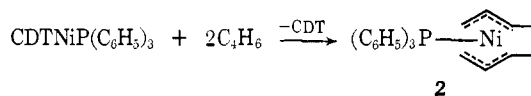
A Model for the Nickel-Catalyzed Cooligomerization of Butadiene with Substituted Alkynes

Sir:

The reaction of butadiene with olefins or alkynes to give ten-membered rings, *e.g.*, 4,5-dimethyl-*cis,cis*-*trans*-1,4,7-cyclodecatriene (**1**) derived from butyne, is



catalyzed by both ligand-free and ligand-modified zerovalent nickel catalysts.¹ This reaction is believed to occur in a stepwise manner and to involve the initial formation of an α,ω -bisallyl- C_8 nickel system which reacts further with the alkyne. The recent isolation of α,ω -octadienediylnickel triphenylphosphine (**2**)² has



provided an opportunity to test this hypothesis.

2 may be prepared by treating the triphenylphosphine adduct of cyclododecatrienickel (CDTNi) with liquid butadiene at -10° .³ The ¹H nmr spectrum⁴ indicates that it contains a symmetrical bis- π -allyl- C_8 chain in contrast to the π -allyl- σ -allyl arrangement observed in systems involving tricyclohexylphosphine.⁵

Dropwise addition of the diethyl ester of acetylenedicarboxylic acid to an ethereal suspension of **2** cooled to -30° results in the formation of a dark red solution

(1) (a) P. Heimbach and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 183 (1969); (b) W. Brenner, P. Heimbach, and G. Wilke, *ibid.*, **727**, 194 (1969); (c) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970); (d) W. Brenner, P. Heimbach, K. J. Ploner, and F. Thömel, *Justus Liebigs Ann. Chem.*, 1882 (1973); (e) P. Heimbach, *Angew. Chem.*, **85**, 1035 (1973).

(2) B. Büssemeier, Doctoral Thesis, University of Bochum, 1973.

(3) All operations were carried out in an argon atmosphere.

(4) Nmr: τ 4.99 (m) meso-H, 6.92 (d, $J_{\text{meso}} = 6.5$ Hz) syn-H, 7.84 (m) CH₂, 8.48 (dd, $J_{\text{meso}} = 12$ Hz, $J_{\text{P}} = 13$ Hz) anti-H; solvent, toluene-d, temperature -10° .

(5) B. Barnett, B. Büssemeier, P. Heimbach, P. J. Jolly, C. Krüger, I. Tkatchenko, and G. Wilke, *Tetrahedron Lett.*, 1457 (1972).

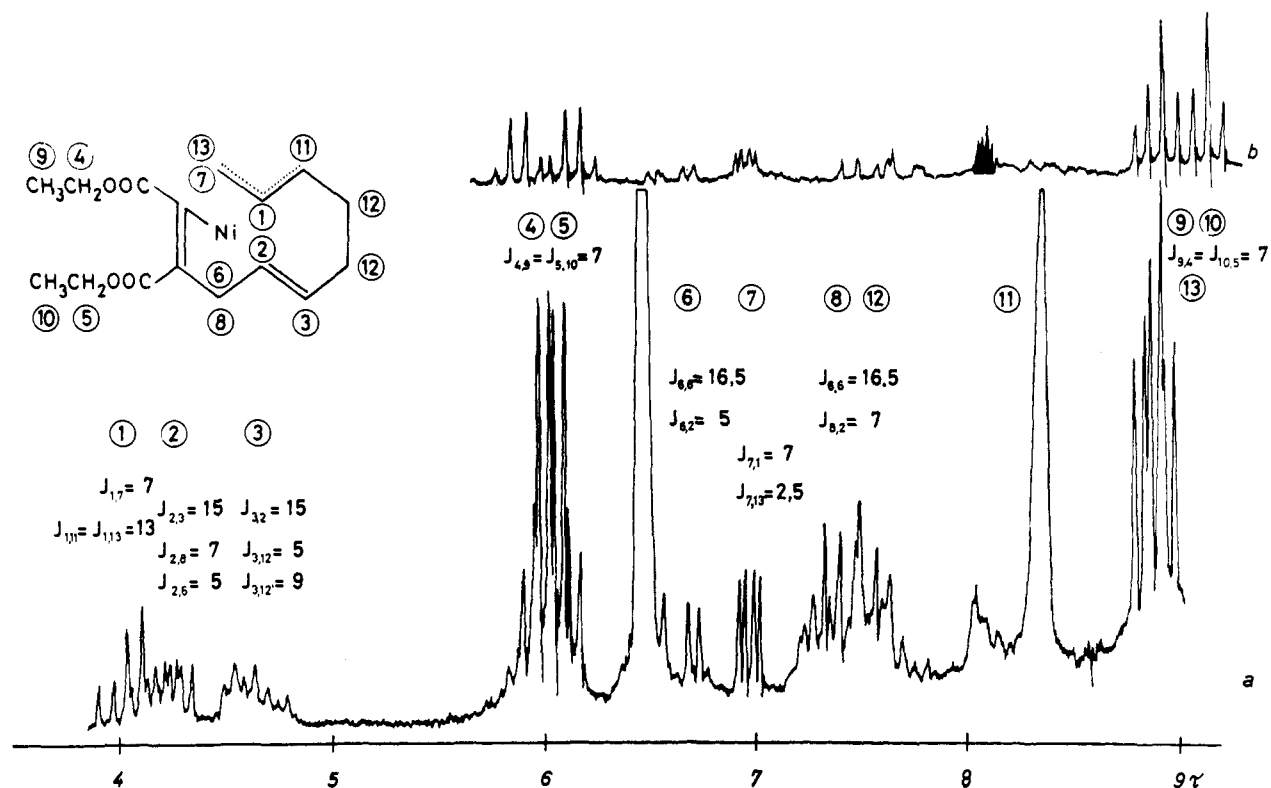
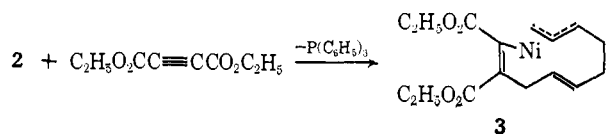


Figure 1. The ^1H nmr spectrum of 3 (100 MHz): (a) CAT in THF-d , (b) in toluene-d .

from which a yellow complex, 3, may be isolated in *ca.*

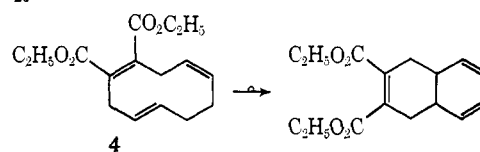
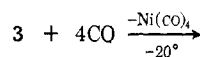


30% yield. Elemental analysis indicates that 3 is free of phosphine and contains two molecules of butadiene and one of alkyne per nickel atom. Mass spectral (MP = 336) and cryoscopic molecular weight determinations (359, benzene) show that 3 is monomeric.

The ^1H nmr spectrum is in agreement with the formulation as a π -allyl- σ -vinyl- C_{10} nickel system (Figure 1). A model indicates that the carbonyl group in the ester function adjacent to the nickel atom can interact with the nickel.⁶

(6) The complexation of an ester function to a metal has been substantiated⁷ by X-ray crystallography for the compound $\text{PdC}_6(\text{CO}_2\text{CH}_3)_4(\text{CO}_2\text{CH}_3)\text{C}(\text{CO}_2\text{CH}_3)\text{Cl}$.

The relevance of 3 to the mechanism of the cooligomerization of butadiene with alkynes is indicated by the reaction with carbon monoxide; 4 mol of CO is absorbed per gram-atom of nickel to give nickel tetracarbonyl and the cyclodecatriene derivative 4 which re-



arranges thermally at 160° to the corresponding divinyl-cyclohexene derivative.^{1d}

(7) D. M. Roe, C. Calvo, N. Krishnamachari, K. Moseley, and P. Maitlis, *J. Chem. Soc., Chem. Commun.*, 436 (1973).

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