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Preliminary Communication

Selectivity of Reactions of Methylhydrazones with Butadiene in the Presence of Palladium and Nickel Complexes.

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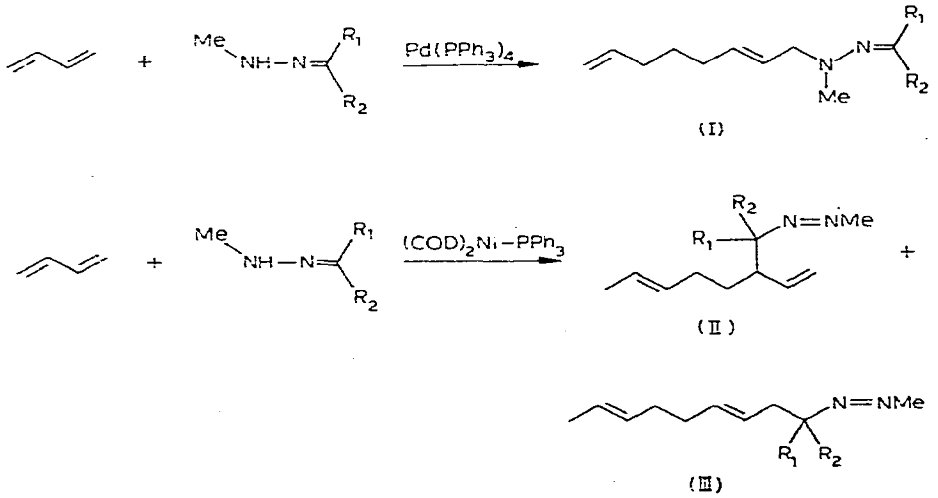
Summary

Reactions of aldehyde and ketone methylhydrazones with butadiene in the presence of palladium complexes have been shown to yield N-octadienylated methylhydrazones. In contrast, in the presence of nickel complexes, a mixture of two isomeric azo-derivatives are formed from two moles of butadiene and one mole of methylhydrazone. The selectivity of these reactions is discussed in terms of the reactivity of the bis-Π-allylmetal intermediates.

Reactions of butadiene with Schiff bases[1] and isocyanates[2] catalysed by palladium complexes have been reported to yield divinyl piperidines and divinyl piperidones, respectively. In contrast, nickel-catalysed reactions of Schiff bases and butadiene gave either octatrienylated amines or octadienylated Schiff bases depending on the substrate structure and the presence of a cocatalyst[3]. Co-oligomerisations of ketazines or aldazines with butadiene catalysed by nickel complexes result in the formation of 1,2-diazacyclododeca-1,5,9-trienes[4]. Both palladium- and nickel-complex catalysed reactions of butadiene with nucleophilic reagents such as amines and active methylene compounds have been extensively studied[5]. We have previously reported the formation of azo-compounds from reactions of phenylhydrazones with butadiene in the presence of nickel and palladium complexes; a small amount of N-alkylation was also observed with the latter complex[6]. We have now shown that, in the reactions of methylhydrazones with butadiene, the formation of azo-compounds or N-alkylation can be completely controlled by the choice of either nickel or palladium complexes.

Typically, a tetrahydrofuran (10 ml) solution of acetaldehyde methylhydrazone (30 mmol), and butadiene (10 ml, 120 mmol) was allowed to react at 110°C for 24 hours in the presence of tetrakis (triphenylphosphine) palladium (0.3 mmol). The product (1) was isolated by distillation, b.p. 98° - 100°/1 mm (89% yield), and characterised by its spectroscopic properties; NMR δ(CDCl$_3$); 1.44(2H quintet,J=7Hz,methylene),1.89 (3H,d,J=6Hz,N=C-CH$_3$),2.04(4H quartet, J=7Hz allylic),2.56(3H,s,N-CH$_3$),3.62(d,2H,J=5Hz,allylic NCH$_2$-),4.9-5.1 (2H,m,C=CH$_2$),5.5-5.6(2H,m,-CH=CH-) 5.7-6.0(1H,m,C=CH) 6.73(1H,quartet, J=6Hz,N=CH); UV(ethanol),240nm (e=6,400).

Alternatively, acetaldehyde methylhydrazone (30 mmols) in diethyl ether was added to a solution of α,ω-octadienediylnickel-triphenylphosphine (30 mmols), butadiene (25 mls, 300 mmols) and diethyl ether (20 mls) under argon at -30°C. After addition of the methylhydrazone the mixture was allowed to reach room temperature and stirred for 20 hours. An aqueous solution of potassium cyanide was added and the products extracted with ether; a mixture of (2) and (3) were obtained by distillation- bp



116° - 118°/2mm. Final separation was achieved by preparative g.l.c. (15 ft, 10% SE30,150°C) and the products characterised by their spectral

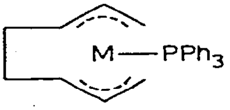
Table

Reactions of methylhydrazones with butadiene

Catalyst	Methylhydrazone		Yield (%)	Products (%)		
	R_1	R_2		(1)	(2)	(3)
$Pd(PPh_3)_4$	H	Me	89	100	-	-
	H	Et	85	100	-	-
	Me	Me	86	100	-	-
	Me	Et	80	100	-	-
$(COD)_2Ni$-PPh_3	H	Me	54	-	68	32
	H	Et	77	-	57	43
	Me	Me	71	-	51	49
	Me	Et	61	-	60	40

properties: (2) δ($CDCl_3$), 1.11(3H,d,J=6Hz,-CH_3),1.61(3H,d,J=7Hz,allylic -CH_3),1.96(4H,m,methylene), 2.50(1H,m,allylic),3.32(1H,quintet,J=7Hz, azo-CH),3.72(3H,s,azo-CH_3) 4.96-5.78(5H,m,vinyl),(3)δ($CDCl_3$),1.20 (3H,d,J=7Hz,CH_3),1.63(3H,d,allylic CH_3),2.02,(4H,m,methylene),2.35(2H, quartet,J=6Hz,allylic CH_2)3.49(1H,m,J=7Hz,azo-CH),3.70(3H,s,azo-CH_3), 4.60(4H,m,vinyl).

In both cases the products must arise by reaction of the methylhydrazone with the intermediate (4). Reactions can then occur at either the carbon or nitrogen of the methylhydrazone. In the presence of the palladium catalyst exclusive nucleophilic attack from the



(IV) (M = Ni, Pd)

nitrogen is observed to yield the alkylated product (1). With the nickel complex the alternative course of reaction, which may be regarded as an electrophilic attack by the π-allyl group on the carbon occurs, followed by hydrogen transfer to yield exclusive formation of the isomeric azo-compounds (2)and (3).

Although this reaction can be alternatively regarded as nucleophilic attack by donation from the nitrogen through the carbon atom onto the π-allyl group, the results would appear to be more consistent with the differing electronic characteristics of the nickel and palladium bis-π-allyl intermediates. In these terms the bis-π-allyl-nickel and -palladium complexes would appear to be more reactive towards electrophilic and nucleophilic attack, respectively.

This conclusion is consistent with other reported nickel and palladium catalysed reactions. Thus, whilst nickel-catalysed reactions of butadiene with ketones proceed readily[7], the analogous reaction with palladium occur much less readily[8,9]. In contrast, bis-π-allyl palladium complexes demonstrate more extensive reactions with nucleophiles than the analogous nickel complex[5].

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10. Satisfactory analytical data was obtained for all new compounds and the infra-red evidence is consistent with *trans*-double bonds in the products, (1), (2)and (3).