Reactions of Phenylhydrazones with Bis-π-allyl-nickel and -palladium Complexes

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Summary The reaction of butadiene and phenylhydrazones in the presence of nickel and palladium complexes has been shown to yield a series of azo-compounds; in the presence of the latter catalyst some alkylation of the hydrazone occurs.

REACTIONS of butadiene with Schiff bases[1] and isocyanates,[2] catalysed by palladium complexes, have been reported to yield divinylpiperidines and divinylpiperidones, respectively. These co-cyclisation reactions have recently been extended to the formation of 1,2-diazacyclododeca-1,5,9-trienes by nickel-catalysed co-oligomerisation of ketazines or aldazines with butadiene.[3] Numerous reports of the reaction of butadiene with amines, catalysed by nickel[4] and palladium[5] catalysts, have appeared.

We now report the co-oligomerisation of butadiene with a series of phenylhydrazones which gives high yields of a mixture of azo-compounds (Scheme). Whilst only (**1**) and (**2**) were formed in the presence of nickel complexes, similar reactions catalysed by a palladium complex yielded an additional product (**3**) although the azo compounds were always predominant in the product mixture† (Table).

Typically, a tetrahydrofuran (10 ml) solution of propanal phenylhydrazone (30 mmol) and butadiene (10 ml) was allowed to react at 110 °C for 24 h in the presence of tetrakis(triphenylphosphine)palladium (0·12 mmol). The product mixture was collected by distillation (110—112 °C at

TABLE

Reactions of phenylhydrazones with butadiene

Catalyst	Yield (%)	Product ratio (**1**)	(**2**)	(**3**)	Phenylhydrazone $R^1R^2C{=}NNHPh$ R^1	R^2
$Pd(PPh_3)_4$	86	36	62	2	Me	H
	95	36	45	19	Et	H
	80	51[a]	15	34	Me	Me
	60	72[a]	17	11	Et	Me
$(cod)_2Ni{-}PPh_3$[b]	82	16	84	—	Me	H
	70	45	55	—	Et	H
	77[c]	36	64	—	Me	Me
	23[d]	57[e]	43	—	Et	Me

[a] Mixture of *cis*- and *trans*-isomer. [b] cod = cyclo-octadiene. [c] 72 h reaction time. [d] Some decomposition of product occurs in the reaction and isolation procedure. [e] Isomeric with (**1**), with internal double bond (MeCH=CH–).

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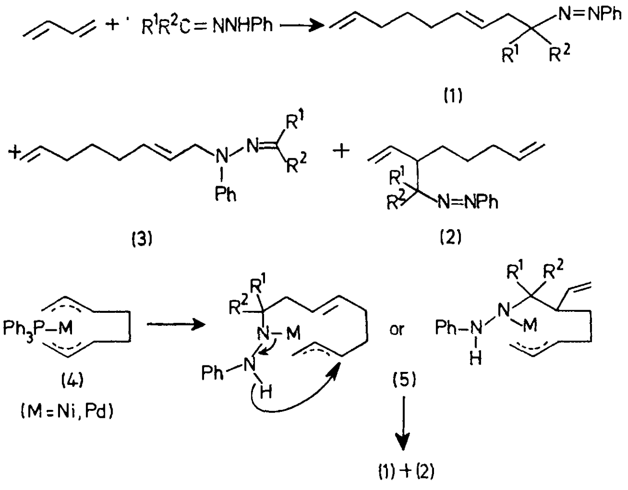
† All assigned structures are fully consistentwith the physical and spectroscopic data obtained.

0·1 mmHg, 7·3 g, 95%) and compounds (**1**)—(**3**) were separated by preparative g.l.c.



SCHEME

The nickel-catalysed reactions were studied under the following conditions. Initially, the phenylhydrazone (23·0 mmol) in diethyl ether (10 ml) was added to αω-octadienediylnickel–(triphenylphosphine) formed from bis(cyclooctadienyl)nickel[6] (3·6 mmol), triphenylphosphine (3·6 mmol), butadiene (15·0 ml), and diethyl ether (10 ml) under argon at −25 °C. After addition of the phenylhydrazone, the mixture was allowed to reach room temperature over 4 h and then stirred for 20 h. An aqueous solution of potassium cyanide was added and the products were extracted with ether and eventually distilled at reduced pressure. Under these conditions a mixture of the two isomeric products (**1**) and (**2**) was formed.

The temperatures at which the palladium and nickel complex catalysed reactions were performed differed widely. The formation of (**3**), in the former reactions, by a Cope rearrangement of (**2**) was considered. This, however, was excluded by experiments in which (**2**) was heated for extensive periods of time in the presence of tetrakis(triphenylphosphine)palladium and under identical reaction conditions; (**2**) remained completely unchanged.

The products must arise from reaction of (**4**) with the phenylhydrazone and the formation of the azo compounds can be regarded as the reaction of a π-allylmetal complex with an electrophilic group[1,2,7] Initial attack to form (**5**) can then be followed by a process which may be formally regarded as a hydride transfer from the nitrogen atom to the second π-allyl group. A reaction scheme involving oxidation–reduction of the metal is also consistent with the catalysis observed in these reactions. With butanone phenylhydrazone in the nickel-catalysed reaction, the hydrogen unit is either transferred directly to the 1-position of the allyl group or subsequent isomerisation of the product occurs catalysed by the nickel complex.[8]

Although (**3**) is only formed in the palladium complex-catalysed reactions, its formation is intriguing. It is clear that a competition between reaction of a π-allyl group at an electrophilic or nucleophilic centre is occurring[9] and that, in this case, the former is favoured.

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