

Reaction of Phenylhydrazones with Bis(π -allyl)-nickel and -palladium Complexes

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The reactions of 2 mol of butadiene and 1 mol of the phenylhydrazones of acetaldehyde, propionaldehyde, acetone, and butanone in the presence of nickel and palladium complexes have been shown to yield a series of two isomeric azo-compounds. In the presence of the latter complexes *N*-octadienylated phenylhydrazones were also formed and the ratio of products varied with the anion of the palladium salt and the nature of the added organophosphorus ligand. With tetrakis(triphenylphosphine)palladium, formation of the azo-adducts was predominant, whereas exclusive alkylation was found in the presence of PdCl₂-PPh₃ and Pd(NO₃)₂-PPh₃. The results of the palladium-complex catalysed reactions have been discussed in terms of the σ - π character of the bis(π -allyl)-palladium intermediates and their reactivity towards electrophilic and nucleophilic reagents. A system containing bis(cyclo-octa-1,5-diene)triphenylphosphinenickel at room temperature gave higher yields than an analogous system in which $\alpha\omega$ -octadienediynickel was produced *in situ* from a nickel(II) salt and tri-isobutylaluminium. This has been shown to be due to the preferred decomposition of one of the isomeric azo-compounds.

NUMEROUS reports of the reactions of butadiene with reagents with nucleophilic or electrophilic character, catalysed by nickel and palladium catalysts, have

appeared.¹ Palladium(0) complexes have been shown to catalyse the reactions of butadiene with alcohols,²⁻⁵ amines,^{5,6} carboxylic acids,^{2,5-8} and active methylene and

¹ R. Baker, *Chem. Rev.*, 1973, **73**, 487.

² E. J. Smutney, *J. Amer. Chem. Soc.*, 1967, **89**, 6793.

³ E. J. Smutney, U.S.P. 3,499,402 (1970).

⁴ S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Letters*, 1967, 2451.

⁵ S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 454.

⁶ Japan Synthetic Rubber Co. Ltd., B.P. 1,178,812/1970.

⁷ W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Letters*, 1970, 3817.

⁸ E. J. Smutney, U.S.P. 3,407,244/1968.

methine compounds.⁹⁻¹¹ The analogous nickel-complex catalysed reactions of butadiene with amines,¹²⁻¹⁴ active methylene compounds,¹⁵ and alcohols¹⁶⁻²⁰ have also been

hydrazone (30 mmol) and butadiene (10 ml) was kept at 110 °C for 6 h in the presence of tetrakis(triphenylphosphine)palladium (0.12 mmol). The product mixture was

TABLE I
Reactions of phenylhydrazones with butadiene^a

Catalyst	Phenylhydrazone		Yield (%)	Products (%)			
	R ¹ R ² C=N·NPh	R ¹ R ²		(1)	(2)	(3)	(4)
Ni(cod) ₂ -PPh ₃	H	Me	82	16	84		
	H	Et	70	45	55		
	Me	Me	77 ^b	36	64		
	Me	Et	23 ^c		43 ^d		
[Pd(PPh ₃) ₄]	H	Me	86 ^e	36	62		2
	H	Et	95 ^f	36	45		19
	Me	Me	80	51 ^g	15		34
	Me	Et	60	72 ^g	17		11
PdCl ₂ -4PPh ₃	H	Me	88 ^h		44		44 ⁱ
	H	Et	76 ^h		43		47 ^j
	Me	Me	62 ^h		55		45
	Me	Et	31 ^h		17		83
[Pd(acac) ₂]-P(C ₆ H ₁₁) ^k	H	Me		14	79		7
[Pd(acac) ₂]-PPh ₃ ^k	H	Me		23	37		40
[Pd(acac) ₂]-P(OPh) ₃ ^k	H	Me			50		50
Pd(NO ₃) ₂ -PPh ₃ ^k	H	Me			100		

^a Palladium-complex catalysed reactions at 110 °C for 24 h; nickel-complex catalysed reactions at room temperature for 24 h. ^b 72 h. ^c Some decomposition of product occurs in the reaction and isolation procedure. ^d (6) (57%) also formed. ^e 6 h. ^f 8 h. ^g Mixture of *cis*- and *trans*-isomers (1 : 1.7). ^h G.l.c. yields using azobenzene as internal standard. ⁱ (5) (12%) also formed. ^j (5) (10%) also formed. ^k Pd : P 1 : 6.

accomplished. In contrast, reactions of butadiene with Schiff's bases²¹ and isocyanates²² 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 azines with butadiene.²³ Nickel-catalysed reactions of Schiff's bases and butadiene have also been shown to yield either octatrienylated amines or octadienylated Schiff's bases depending on the substrate structure and the presence of a co-catalyst.²⁴

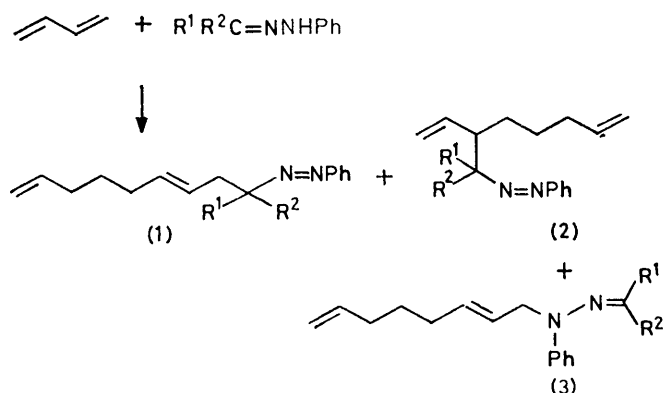
In this paper we report that the reaction of butadiene with phenylhydrazones, in the presence of nickel and palladium complexes, yields a series of azo-compounds and that, in the presence of the latter catalyst, some alkylation of the hydrazone occurs.²⁵ Further, the ratio of these products can be changed with the nature of the palladium salt and the ligand employed.

RESULTS AND SPECTRA

Palladium-complex Catalysed Reactions.—Typically a tetrahydrofuran (10 ml) solution of acetaldehyde phenyl-

- ⁹ T. M. Shryne, U.S.P. 3,562,314/1971.
¹⁰ G. Hata, K. Takahashi, and A. Miyake, *Chem. and Ind.*, 1969, 1836.
¹¹ G. Hata, K. Takahashi, and A. Miyake, *J. Org. Chem.*, 1971, **36**, 2116.
¹² R. Baker, D. E. Halliday, and T. N. Smith, *J.C.S. Perkin II*, 1974, 1511.
¹³ J. Kiji, E. Sasakawa, K. Yamamoto, and J. Furukawa, *J. Organometallic Chem.*, 1974, **77**, 125.
¹⁴ D. Rose, *Tetrahedron Letters*, 1972, 4197.
¹⁵ R. Baker, A. H. Cook, and T. N. Smith, *J.C.S. Perkin II*, 1974, 1517.
¹⁶ J. Beger, C. Duschek, and H. Fullbrier, *J. prakt. Chem.*, 1974, **316**, 26.
¹⁷ D. Commereuc and V. Chauvin, *Bull. Soc. chim. France*, 1974, 652.

collected by distillation (86% yield) and compounds (1)–(3) were separated by preparative g.l.c. (Table 1).



The products were identified on the basis of their spectral characteristics (Table 2). The two monosubstituted double bonds of (2) have vinylic protons which exhibit overlapping AB quartets in the n.m.r. spectra. A signal at δ 2.6 was attributed to an allylic methine and a resonance at δ 3.7 was assigned to the methine adjacent to the azo-function [which occurred only in the spectra of (2) obtained from the

- ¹⁸ T. C. Shields and W. E. Walker, *Chem. Comm.*, 1971, 193.
¹⁹ T. Ohata, K. Ebina, and N. Yamaziki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1321.
²⁰ F. Weigert and W. C. Drinkard, *J. Org. Chem.*, 1973, **38**, 335.
²¹ J. Kiji, K. Yamamoto, H. Tomita, and J. Furukawa, *J.C.S. Chem. Comm.*, 1974, 506.
²² K. Ohno and J. Tsuji, *Chem. Comm.*, 1971, 247.
²³ P. Heimbach, B. Hugelin, H. Peter, A. Roloff, and E. Troxler, *Angew. Chem. Internat. Edn.*, 1976, **15**, 49.
²⁴ P. Heimbach, B. Hugelin, E. F. Nabbefeld, D. Reinehr, A. Roloff, and E. Troxler, *Angew. Chem. Internat. Edn.*, 1977, **16**, 253.
²⁵ R. Baker, M. S. Nobbs, and D. T. Robinson, *J.C.S. Chem. Comm.*, 1976, 723.

aldehyde phenylhydrazones]. The presence of a phenylazo-function was confirmed by u.v. spectra, which showed an $n \rightarrow \pi^*$ absorption at 400 nm (ϵ 130) and a $\pi \rightarrow \pi^*$ absorption at 260 nm (ϵ 9 000). Terminal olefin protons (δ 4.9—5.1 and 5.6—6.0) and signals due to an internal double bond (δ ca. 5.4—5.6) were apparent in the n.m.r. spectra of (1). The structure of (3) was clearly differentiated from those of (1) and (2) by its spectral details.

For the aldehyde phenylhydrazones the disubstituted double bond was considered to be *trans* on the basis of a strong i.r. peak at 970 cm^{-1} and the absence of an absorption at 730 cm^{-1} . The compound also appeared to be homogeneous (g.l.c.). However, the product (1) from reaction of the ketone phenylhydrazones was shown to be a mixture, since *cis*- and *trans*-isomers (1:1.7) were separated by g.l.c. The *cis*-isomer showed ν_{max} 730 cm^{-1} . The alkylated

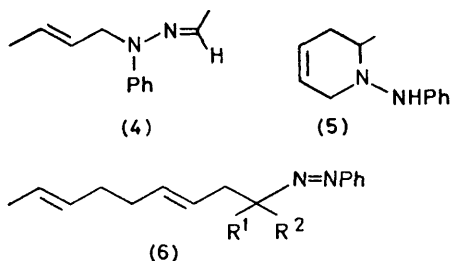
TABLE 2
Spectroscopic details for products (1)—(4) *

	$\delta(\text{CDCl}_3)$	m/e	$\nu_{\text{max.}}/\text{cm}^{-1}$	$\lambda_{\text{max.}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
(1a)	1.36 (3 H, d, J 7 Hz, CH_3)	242 (12%, M)	3 070m	400 (175)
	1.40 (2 H, quintet, J 7 Hz, CH_2)	105 (57%)	1 640s	266 (9 120)
	2.02 (4 H, q, J 7 Hz, allyl CH_2)	77 (100%)	995m	
	2.52 (2 H, q, J 6 Hz, allyl CH_2)	55 (52%)	970s	
	3.82 (1 H, m, J 7 Hz, azo-CH)	41 (48%)	915s	
	4.9—5.1 (2 H, m, $=\text{CH}_2$)			
	5.4—5.5 (2 H, m, vinyl)			
	5.6—6.0 (1 H, m, $=\text{CH}$)			
	7.4—7.7 (5 H, m, Ph)			
	1.29 (3 H, d, J 7 Hz, CH_3)	242 (6%, M)	3 080m	400 (175)
	1.1—1.7 (4 H, m, CH_2)	105 (46%)	1 640m	266 (9 120)
1.9—2.1 (2 H, br q, allyl CH_2)	77 (100%)	1 000m		
2.4—2.8 (1 H, m, allyl CH)	55 (49%)	915s		
3.66 } (quintet, J 7 Hz, azo-CH)				
3.78 }				
4.9—5.2 (4 H, m, $=\text{CH}_2$)				
5.6—6.0 (2 H, m, $=\text{CH}$)				
7.4—7.7 (5 H, m, Ph)				
(3a)	1.41 (2 H, quintet, J 7 Hz, CH_2)	242 (35%, M)	3 070m	279 (20 800)
	2.02 (3 H, d, J 5 Hz, CH_3)	133 (57%)	1 640m	
	1.9—2.1 (4 H, m, allyl CH_2)	105 (61%)	995m	
	3.30 [2 H, d, J 3 Hz, allyl $\text{CH}_2(\text{N})$]	77 (100%)	970s	
	4.9—5.1 (2 H, m, $=\text{CH}_2$)	41 (46%)	915s	
	5.4—5.5 (2 H, m, vinyl)			
	5.6—6.0 (1 H, m, vinyl)			
	6.7—7.4 (6 H, m, Ph and $\text{N}=\text{CH}$)			
	1.67 (3 H, d, J 6 Hz, CH_3)	188 (100%, M)	3 060m	279 (17 700)
	2.01 [3 H, d, J 6 Hz, $\text{N}=\text{C}(\text{CH}_3)$]	133 (72%)	1 600s	
4.26 [2 H, br d, allyl $\text{CH}_2(\text{N})$]	77 (73%)	970s		
5.4—5.6 (2 H, m, vinyl)	105 (69%)			
6.7—7.3 (6 H, m, Ph, $\text{N}=\text{CH}$)				
(1c)	1.16 (3 H, s, CH_3)	256 (2%, M)	3 080m	414 (146)
	1.18 (3 H, s, CH_3)	95 (56%)	1 645m	263 (8 800)
	1.39 (2 H, quintet, J 7 Hz, CH_2)	69 (100%)	1 000m	
	(<i>trans</i>) 2.45 (2 H, d, J 7 Hz, allyl CH_2) }	55 (43%)	975s	
	(<i>cis</i>) 2.51 (2 H, d, J 6 Hz, allyl CH_2) }	41 (35%)	915s	
	4.9—5.1 (2 H, m, $=\text{CH}_2$)		730m	
	5.4—5.5 (2 H, m, vinyl)			
	5.6—5.9 (1 H, m, vinyl)			
	7.4—7.7 (5 H, m, Ph)			
	1.16 (3 H, s, CH_3)	256 (3%, M)	3 070m	414 (143)
1.20 (3 H, s, CH_3)	148 (100%)	1 645m	263 (8 500)	
1.96 (2 H, br s, allyl CH_2)	92 (92%)	1 000m		
2.49 (1 H, d of t, J 9 and 3 Hz, allyl CH)	65 (44%)	915s		
4.9—5.1 (4 H, m, $=\text{CH}_2$)				
5.5—5.9 (2 H, m, vinyl)				
7.4—7.7 (5 H, m, Ph)				
(3c)	1.44 (2 H, quintet, J 7 Hz, CH_2)	256 (44%, M)	3 070m	280 (3 400)
	1.92 [3 H, s, $\text{N}=\text{C}(\text{CH}_3)$]	147 (100%)	1 645m	253 (9 800)
	2.14 [3 H, s, $\text{N}=\text{C}(\text{CH}_3)$]	106 (98%)	1 000m	
	2.04 (2 H, q, J 7 Hz, CH_2)	77 (48%)	975m	
	3.96 [2 H, d, J 4 Hz, allyl $\text{CH}_2(\text{N})$]		915s	
	4.9—5.1 (2 H, m, $=\text{CH}_2$)			
	5.5—5.6 (2 H, m, vinyl)			
	5.7—6.0 (1 H, m, vinyl)			
	6.8—7.3 (5 H, m, Ph)			
	1.68 (3 H, d, J 6 Hz, CH_3)	202 (63%, M)	3 060m	280 (2 950)
1.90 [3 H, s, $\text{N}=\text{C}(\text{CH}_3)$]	106 (100%)	1 640m	252 (8 900)	
2.14 [3 H, s, $\text{N}=\text{C}(\text{CH}_3)$]	147 (63%)	970s		
3.96 [2 H, d, J 4 Hz, $\text{CH}_2(\text{N})$]	76 (33%)			
5.5—5.7 (2 H, m, vinyl)				
6.7—7.3 (5 H, m, Ph)				

* Spectra for (1b)—(4b) and (1d)—(4d) are similar.

phenylhydrazone (3) appeared to be solely the *trans*-isomer on the same consideration.

In another series of experiments the catalyst system was changed to include a series of palladium salts in the presence of various organophosphorus ligands (Table 1). The product ratio was dependent upon the nature of the ligand and the anion of the palladium salt. In particular, exclusive formation of (3) was found with palladium nitrate as catalyst. A further product (4) was also formed from reaction of 1 mol of butadiene and phenylhydrazone in the presence of two other catalyst systems and, in the case of tetrakis(triphenylphosphine)palladium chloride, a small amount of (5), which was shown to arise from a thermal



reaction, was also formed. Whilst the reactions of only one phenylhydrazone is reported similar changes were also observed with the other phenylhydrazones.

Nickel-complex Catalysed Reactions. The phenylhydrazone (23.0 mmol) in diethyl ether (10 ml), was added to a solution of $\alpha\omega$ -octadienediyl(triphenylphosphine)nickel at -20°C , prepared *in situ* from bis(cyclo-octadiene)nickel²⁶ (3.64 mmol), triphenylphosphine (3.60 mmol), and butadiene (15 ml). After addition of the phenylhydrazone, the solution was warmed to room temperature over 4 h and stirred overnight. An aqueous solution of potassium cyanide was added and the products were extracted and distilled at reduced pressure to yield a mixture of (1) and (2), which were separated by preparative g.l.c. (Table 1). The absence of (3) in the product mixtures of these reactions was noted. On reaction of butan-2-one phenylhydrazone the double-bond isomer (6) was formed and (1) was absent.

An alternative series of nickel-catalysed reactions was also investigated. A red solution of $\alpha\omega$ -octadienediyl(triphenylphosphine)nickel was prepared from bis(acetylacetonato)nickel (3.87 mmol), triphenylphosphine (3.9 mmol), and butadiene (2.0 ml) in toluene (2 ml), by adding tri-isobutylaluminium (7.7 mmol) in toluene (10 ml) at 0° . The solution was syringed under argon into a Carius tube containing the phenylhydrazone (23.0 mmol) in toluene (6.0 ml). Butadiene (15.0 ml) was distilled into the tube, and after sealing, the reaction mixture was heated at 75°C for a prescribed time (Table 3).

Under these conditions the reactions appeared to proceed in a more selective manner although lower yields were obtained. Except for the reaction of acetaldehyde phenylhydrazone, the predominant or sole product was (6). This could be easily distinguished from (1) and (2) since (6) had no terminal olefinic protons and a new resonance at δ 1.7 was assigned to a vinylic methyl group. In all cases, the stereochemistry of the double bonds of (6) was assigned as *trans* on the basis of i.r. evidence.

²⁶ R. A. Schunn, *Inorg. Synth.*, 1974, **15**, 5.

²⁷ R. Baker, B. N. Blackett, R. C. Cookson, R. C. Cross, and D. P. Madden, *J.C.S. Chem. Comm.*, 1972, 343.

TABLE 3

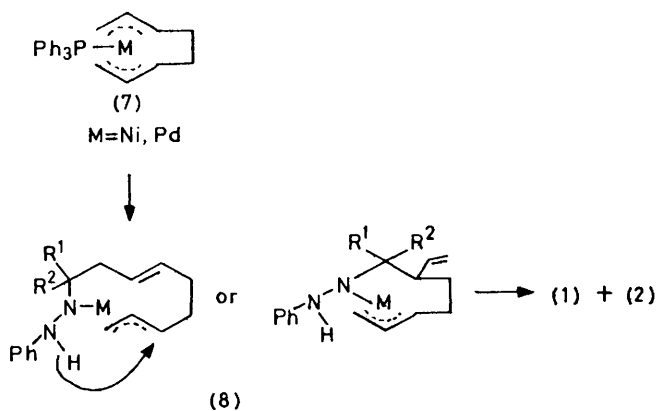
Reactions of phenylhydrazones with butadiene at 75° *

Phenylhydrazone R ¹ R ² C:N-NHPh	Reaction time/h	Yield (%)	Products (%)		
			(1)	(2)	(3)
Me H	1	47	67	33	
	3	59	100		
	15	34	100		
Et H	3	65		45	55
	6	63		18	82
	15	43			100
Me Me	3	55			100
	6	65			100
	15	67			100
Et Me	3	40			100
	6	40			100
	15	65			100

* $\alpha\omega$ -Octadienediylnickel (ca. 3.9 mmol), triphenylphosphine (3.9 mmol), phenylhydrazone (23.0 mmol), toluene (16 ml), butadiene (15.0 ml, 180 mmol).

DISCUSSION

The products (1)—(3) (Table 1) must arise by reaction of the phenylhydrazone with the intermediate (7). Formation of the azo-compounds (1) and (2) can be regarded as reaction of a π -allylmetal complex with an electrophilic group. Initial attack to form (8) 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. Alternative processes involving hydrogen transfer *via* the metal cannot be excluded. The first step is probably analogous to that found in other metal-complex catalysed reactions of butadiene with reagents having electrophilic character such as Schiff's bases^{21,24} and isocyanates.²² The aminonickelate intermediate (8) proposed is analogous to the intermediate proposed in the reactions of π -allylnickel complexes with aldehydes.^{27,28} Whilst similar azo-products are formed in the nickel- and palladium-catalysed reactions, the product (6), formed particularly in the former reaction at 75°C , is probably obtained by nickel-complex catalysed olefin isomerisation²⁹ of the initial product (1).

The product (3) is only formed in the palladium-complex catalysed reactions and clearly results from a

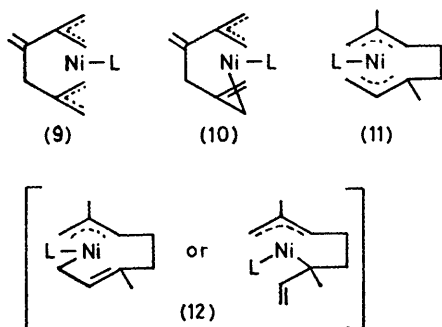
²⁸ P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1969, **8**, 29.

²⁹ P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' vol. II, Academic Press, London, 1975, pp. 54—61.

nucleophilic reaction of the phenylhydrazone with the π -allylmetal complex (7). This process is analogous to similar reactions of π -allylmetal complexes with amines.^{5,6,12-14} In the present palladium-complex catalysed reactions it appears that competition is occurring between reaction of the π -allyl group at an electrophilic and at a nucleophilic centre. With $[\text{Pd}(\text{PPh}_3)_4]$ as catalyst, the former process is favoured.

The structural relationship of the azo-product (2) and the hydrazone adduct (3) might have suggested the interconversion of the two by a palladium-catalysed [3,3] Cope rearrangement. This possibility was excluded by experiments in which (2) and (3) were heated under identical conditions with palladium chloride-triphenylphosphine and with tetrakis(triphenylphosphine)palladium but no interconversion was observed.

We have reported previously that considerable regio-specificity was observed in the reaction of unsymmetrical bis(π -allyl)nickel intermediates.³⁰ Reactions of the bis(π -allyl)nickel complexes, derived from isoprene (11) and allene (9), with active methylene compounds, amines,



and aldehydes, have indicated a selectivity which has been related to the σ - π character^{31,32} of the structure of the complexes (10) and (12). Predominant products from reaction of amines and active methylene compounds with (10) and (12) appeared to be derived by attack at the π -allyl site whilst preferential reaction of aldehydes took place at the σ -allyl group of the nickel complexes. Whilst the differences in the nickel- and palladium-complex systems cannot be discussed in these terms, the changes in product ratios with the different palladium salts and ligands (Table 1) could reflect the differing σ - π character of the intermediate bis(π -allyl)palladium complexes. Thus with bis(acetylacetonato)palladium as catalyst the change in product ratio from predominant formation of (1) and (2) to complete formation of (3) and (4) as the ligand changes in the order, tris(cyclohexyl)phosphine, triphenylphosphine, and triphenyl phosphite could reflect a decreasing σ -character of the bis(π -allyl)palladium intermediate. Good electron-donating ligands such as tris(cyclohexyl)phosphine have

³⁰ R. Baker, A. H. Cook, and M. J. Crimmin, *J.C.S. Chem. Comm.*, 1975, 727.

³¹ B. L. Barnett, C. Kruger, and Y. H. Tsay, *Angew. Chem. Internat. Edn.*, 1972, **11**, 137.

³² B. Barnett, B. Bussemeier, P. Heimbach, P. W. Jolly, C. Kruger, L. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, 1457.

been shown to favour the σ - π form of allylmetal intermediates;³³⁻³⁵ under these conditions product formation resulting from initial attack on the electrophilic centre of the phenylhydrazone appears to be favoured. Conversely, organo-phosphites favour the π -form of allylmetal intermediates, and formation of (3) and (4) by reaction at the nucleophilic nitrogen of the phenylhydrazone occurs in the presence of triphenyl phosphite. Although (1) and (2) may also be considered to arise by nucleophilic attack through the carbon atom of the phenylhydrazone, this does not appear to be consistent with the changing product ratios with the differing palladium salts and ligands.

The formation of (4) clearly involves 1 mol of butadiene and the phenylhydrazone. This product is only found when palladium chloride and bis(acetylacetonato)-palladium are used in the catalyst mixture. The formation of a π -allylpalladium complex from 1 mol of butadiene requires the involvement of a hydrido-palladium intermediate. Formation of the intermediate appears to be significant only in the presence of these two palladium salts. This is consistent with observations reported by Tsuji and his co-workers^{36,37} for the carbonylation reactions of butadiene; in the presence of palladium chloride and triphenylphosphine in ethanol, ethyl pent-3-enoate is formed in good yield. With other palladium salts, which are halide-free, the product is nona-3,8-dienoate. It was suggested that a hydrido-palladium complex is formed under the former conditions by oxidative addition of hydrogen chloride to the palladium, which can then lead to monomeric π -allylic complex.

The two different nickel-complex catalyst systems were employed at two different temperatures. At 75 °C, particularly at longer reaction times, a single product (1) or (6) (Table 3) was obtained. This was shown, however, to be due to the decomposition of (2) under the more vigorous reaction conditions. In a control experiment, butadiene was passed into a solution of α - ω -octadienediynickel, triphenylphosphine, acetaldehyde phenylhydrazone, and an internal standard, diphenylmethane, and the solution was maintained at 75 °C. G.l.c. showed that the amounts of both (1) and (2) increased in the earlier stages but a steady fall in the absolute amount of (2) then occurred (Table 4). At longer reaction times decomposition of (1) was also significant. No decomposition products were identified.

The additional product (5), produced under conditions where longer reaction times were required, has been shown to be a thermal addition product of butadiene and the aldehyde phenylhydrazones. This reaction was further investigated and shown to proceed readily

³³ G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem. Internat. Edn.*, 1976, **15**, 49.

³⁴ L. A. Leites, V. T. Aleksanyan, S. S. Bukalor, and A. Z. Rubezhow, *Chem. Comm.*, 1971, 265.

³⁵ K. Vrieze, C. Maclean, P. Crossee, and C. W. Hilbers, *Rec. Trav. chim.*, 1966, **85**, 1077.

³⁶ S. Hosaka and J. Tsuji, *Tetrahedron*, 1971, **27**, 3821.

³⁷ J. Tsuji, Y. Mori, and M. Hara, *Tetrahedron*, 1972, **28**, 3721.

at 160 °C, in the absence of palladium-complex catalysts, to yield two products (5) and (14) in 73% yield. The

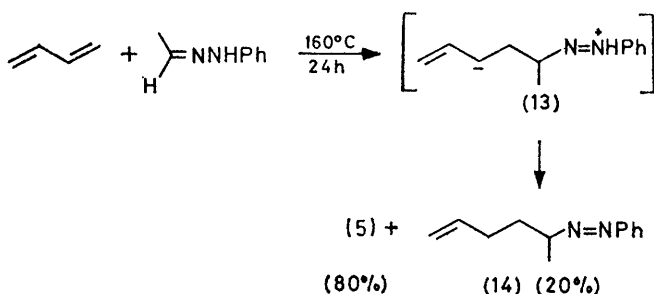
TABLE 4

Reaction of acetaldehyde phenylhydrazone and butadiene at 75 °C,^a analysis of product mixture by g.l.c. and internal standard

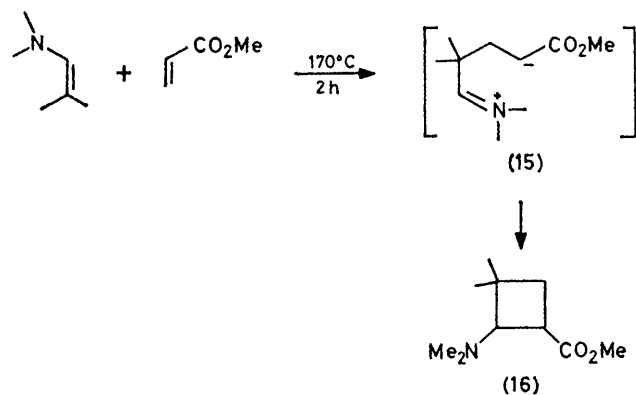
Time (h)	Hydrazone conversion (%)	(1) ^b	(2) ^b	(1)/(2)
0.08	11	0.11	0.22	0.5
0.25	37	0.57	0.68	0.84
0.50	54	0.80	0.61	1.3
0.75	62	0.85	0.51	1.7
1.00	83	0.90	0.41	2.2
1.50	95	1.00	0.23	4.3
2.0	c	0.84	0.16	5.2
2.5	c	0.81	0.11	7.4
3.0	c	0.62	0.07	8.9

^a $\alpha\omega$ -Octadienediylnickel (1.93 mmol), triphenylphosphine (1.93 mmol), acetaldehyde phenylhydrazone (15.0 mmol), diphenylmethane (1.0 ml); butadiene passed in at atmospheric pressure, 75 °C. ^b Relative to diphenylmethane as internal standard. ^c Measurement of peak area became too inaccurate.

intermediate (13) could be considered to lead to the two products by either proton transfer or nucleophilic attack of the allylic anion at the protonated azo-moiety,



respectively. This reaction is analogous to the thermal reaction of enamines with substituted olefins, leading to



substituted cyclobutanes (16), for which a similar dipolar intermediate (15) was proposed.³⁸

³⁸ K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, 1961, **26**, 625.

³⁹ W. G. Kenyon and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 292.

Hydrazone can be alkylated by the addition of an alkyl halide to the sodium salt formed by reaction of the hydrazone with sodamide. Although it was shown that the charge was distributed through the hydrazone moiety, alkylation proceeded exclusively on the nitrogen in all cases.³⁹ The present reaction provides one of the few examples of hydrazones undergoing reaction at the α -carbon atom.⁴⁰

EXPERIMENTAL

Bis(cyclo-octa-1,5-diene)nickel,²⁶ tetrakis(triphenylphosphine)palladium,⁴¹ and the phenylhydrazones⁴² were prepared by reported procedures. Solvents were dried by distillation from lithium aluminium hydride.

Palladium-complex Catalysed Reactions.—To a Carius tube (100 ml) flushed with nitrogen were added tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol), acetaldehyde phenylhydrazone (4 g, 30 mmol), and tetrahydrofuran (10 ml). Butadiene (10 ml, 120 mmol) was distilled into the tube, which was sealed and heated to 110 °C for 6 h. The mixture was analysed by g.l.c. (5 ft; 10% SE 30), and distillation gave (1)—(3) (110—112°/0.3 mmHg; 6.1 g, 86%). Final separation was achieved by preparative g.l.c. (10 ft; 25% SE 30; 230 °C) to yield the three products, which were distilled (bulb-to-bulb) before final spectroscopic analysis (Table 2). Similar procedures were used for the other phenylhydrazones except that the normal reaction times were 24 h and the ratio of phenylhydrazone to palladium complex was 100:1. B.p.s and analytical data of the products are recorded in Table 5.

Nickel-complex Catalysed Reactions.—A solution of freshly distilled phenylhydrazone (23.0 mmol) in diethyl ether (10 ml) was added to $\alpha\omega$ -octadienediyl(triphenylphosphine)nickel prepared by the addition of butadiene (15 ml) to an ethereal solution (10 ml) of bis(cyclo-octa-1,5-diene)nickel (1 g, 3.64 mmol) and triphenylphosphine (0.95 g, 3.60 mmol) at -20 °C. The mixture was allowed to warm to room temperature over 4 h and stirred for 20 h. Potassium cyanide (1.5 g per g of Ni) in water (50 ml) was added and the mixture stirred well until the yellow mixture of potassium tetracyanonickelate was obtained (1—2 h). The aqueous phase was extracted with ether and the combined ether solutions were washed with water and dried (CaSO₄). Products were obtained as above.

For the reactions at 75 °C, bis(acetylacetonato)nickel (1 g, 3.87 mmol) and triphenylphosphine (1.11 g, 4.2 mmol) in toluene (5.0 ml) were alternately evacuated and flushed several times with argon in a three-necked, round-bottomed flask. Butadiene (1.0 ml) was distilled into the flask and tri-isobutylaluminium (1.2 g, 6.1 mmol) in toluene (2.0 ml) was added dropwise at 0 °C; a deep red solution was formed. This reagent was added by syringe under argon to a Carius tube containing the phenylhydrazone (23.0 mmol) and butadiene (15 ml) in toluene (6.0 ml) and the mixture was heated for the required time at 75 °C. The products were isolated as previously described to yield (1) and (2) from reaction of acetaldehyde phenylhydrazone and (6) from propionaldehyde, acetone, and butanone phenylhydrazones. The b.p.s of (6b), (6c), and (6d) were 110—112° (0.1 mmHg), 112—115° (0.1 mmHg), and 115—121 °C (0.1 mmHg),

⁴⁰ J. Buckingham, *Quart. Rev.*, 1969, **23**, 37.

⁴¹ D. R. Coulson, *Inorg. Synth.*, 1971, **13**, 121.

⁴² 'Dictionary of Organic Compounds,' 4th edn., 1965, Eyre and Spottiswood, London, vol. 1.

TABLE 5
 Analytical and b.p. data

Product	B.p. (°/mmHg)	Formula	Required (%)			Found (%)		
			C	H	N	C	H	N
(1a), (2a)	110—112/0.3	C ₁₆ H ₂₂ N ₂	79.3	9.15	11.55	79.35	9.05	11.65
(3a)	110—112/0.3	C ₁₆ H ₂₂ N ₂	79.3	9.15	11.55	79.45	9.3	11.55
(4a)	60/0.1 ^a	C ₁₂ H ₁₆ N ₂	76.55	8.55	14.9	76.55	8.5	14.7
(5a)	55—56° (m.p.)	C ₁₂ H ₁₆ N ₂	76.55	8.55	14.9	76.55	8.65	14.85
(14)	60/0.1 ^a	C ₁₂ H ₁₆ N ₂	76.55	8.55	14.9	76.8	8.6	15.15
(1b), (2b)	110—112/0.1	C ₁₇ H ₂₄ N ₂	79.65	9.45	10.95	79.65	9.2	11.1
(3b)	110—112/0.1	C ₁₇ H ₂₄ N ₂	79.65	9.45	10.95	79.75	9.4	10.65
(4b)	60/0.1 ^a	C ₁₃ H ₁₈ N ₂	77.2	8.95	13.85	77.95	8.8	13.7
(5b)	60/0.1 ^a	C ₁₃ H ₁₈ N ₂	77.2	8.95	13.85	77.15	8.95	14.2
(1c), (2c)	104—106/0.1	C ₁₇ H ₂₄ N ₂	79.65	9.45	10.95	79.6	9.45	10.8
(3c)	104—106/0.1	C ₁₇ H ₂₄ N ₂	79.65	9.45	10.95	79.55	9.6	10.95
(4c)	60/0.1 ^a	C ₁₃ H ₁₈ N ₂	77.2	8.95	13.85	77.55	8.9	13.3
(1d), (2d)	90—92/0.03	C ₁₆ H ₂₀ N ₂		M ⁺ 270.2096 ^b			M ⁺ 270.2098 ^b	
(3d)	90—92/0.03	C ₁₆ H ₂₀ N ₂		M ⁺ 270.2096 ^b			M ⁺ 270.2098 ^b	
(4d)	60/0.1 ^a	C ₁₄ H ₂₀ N ₂	77.75	9.3	12.95	78.55	9.2	12.5

^a Bulb to bulb distillation after preparative g.l.c. ^b Products too unstable for elemental analysis, high-resolution mass spectra results quoted.

respectively. The spectral characteristics were similar in many ways to those of (1) and (2); details of (6b) (as an example) are as follows: $\delta(\text{CDCl}_3)$ 0.88 (3 H, t, J 7 Hz, CH₃), 1.3 (2 H, m, CH₂), 1.62 (3 H, br s, CH₃), 2.05 (4 H, m, allylic CH₂), 2.5 (2 H, q, J 7 Hz, methine), 5.6 (4 H, m, vinylic), and 7.3—7.85 (5 H, m, aromatic); m/e 256 (4%, M), 95(51%), 77(100%), 67(36%), and 55(91%); ν_{max} 1 640m, 970s, and 915m cm⁻¹; λ_{max} 263 (ϵ 6 950) and 397 nm (126).

Reaction of Acetaldehyde Phenylhydrazone with Butadiene.—Acetaldehyde phenylhydrazone (0.4 g, 3 mmol) was heated at 160 °C for 24 h with butadiene (1.5 ml, 18 mmol) in tetrahydrofuran (1 ml) in a Carius tube. The products were bulb-to-bulb distilled [*ca.* 60 °C (0.1 mmHg)] to yield a 4 : 1 mixture of (5) and (14) (0.41 g, 73%). Separation by preparative g.l.c. (15 ft; 10% SE 30; 190 °C) yielded (5) [$\delta(\text{CDCl}_3)$ 1.11 (3 H, d, J 6 Hz, CH₃), 2.0—2.2 (2 H, m, allylic CH₂), 2.93 (1 H, sextet, J 6 Hz, NCH), 3.29 (2 H, d of

d, J 6 and 2 Hz, NCH₂), 4.53 (1 H, s, NH), 5.5—5.9 (2 H, m, vinyl), and 6.6—7.2 (5 H, m, Ph); ν_{max} 3 320m, 3 020m, and 670m cm⁻¹; m/e 188(67%, M), 175(90%), 93(61%), 92(100%), and 65(60%); λ_{max} 244 (ϵ 11 600) and 291 nm (1 620)]; and (14) [$\delta(\text{CDCl}_3)$ 1.35 (3 H, d, J 6 Hz, CH₃), 1.6—2.2 (4 H, m, CH₂), 3.78 (1 H, sextet, J 6 Hz, azo-CH), 4.9—5.1 (2 H, m, vinylic CH₂), 5.6—6.0 (1 H, m, vinylic CH), and 7.4—7.7 (5 H, m, Ph); ν_{max} 3 080m, 1 640m, 1 000m, and 915s cm⁻¹; m/e 105(41%), 77(100%), 55(31%), 41(32%), and 188(9%, M); λ_{max} 400 (ϵ 152) and 264 nm 9 000)].

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