Reaction of Amines with 1,3-Dienes catalysed by Nickel Complexes

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Reactions of morpholine, piperidine, pyrrolidine, di-n-propylamine, n-butylamine, aniline, and *p*-anisidine with buta-1,3-diene in the presence of catalytic quantities of nickel acetylacetonate and di-isopropoxyphenylphosphine have been studied. Mixtures of 1 : 1 (butenyl) and 2 : 1 (octadienyl) amine products are produced and the reaction with morpholine has been studied in detail to examine the factors determining the product mixtures. Butenyl adduct formation is favoured by (a) a 3 : 1 ratio of phosphine–nickel salt concentration, (b) use of nickel halides with ethanol solvent, and (c) a low effective concentration of butadiene. A product mixture containing 86% octadienyl adduct was obtained by using a preformed Ni^0 complex $Ni[P(OPh)_3]_4$. Reaction of morpholine and isoprene gave mainly a 1 : 1 adduct and small amounts of a 2 : 1 adduct; a similar reaction with *trans*-piperylene gave only a 1 : 1 adduct. The mechanism of the reactions is discussed in terms of formation of the butenyl and octadienyl adduct formation from π-allylnickel and bis-π-allylnickel complexes. The use of cocatalysts such as sodium borohydride in the reactions is discussed. Isomerisation of branched to linear butenyl adduct has been demonstrated to occur.

REACTIONS between amines and 1,3-dienes have previously been reported with palladium [1-3] and rhodium [4] complexes yielding mixtures of octadienyl- and butenylamine derivatives. We have been investigating the synthetic use of nickel complexes in reactions of active hydrogen compounds and 1,3-dienes. Our interest has been in the factors which govern the product distribution between 1 : 1 and 1 : 2 adducts and the mechanism of the catalysed processes. It has been demonstrated that clear differences in reaction are shown by the change in metal from previous work, which is a reflection of the basicity and co-ordination properties of nickel. Product distribution has also been shown to be dependent on solvent, mode of reduction, the nature of the nickel salt, and the presence of a cocatalyst in solution. This paper reports a study of reactions between primary and secondary amines and 1,3-dienes with nickel complex catalyst systems.[5,6]

RESULTS

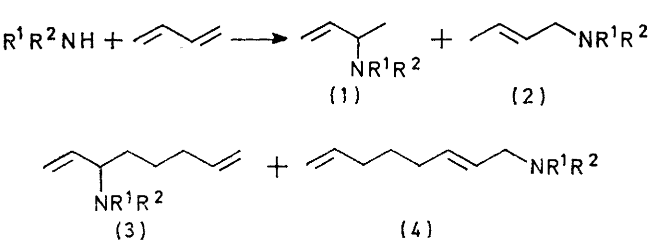
A series of amines (50 mmol) were treated with butadiene (150 mmol) in the presence of nickel acetylacetonate (1 mmol) and di-isopropoxyphenylphosphine (1·1 mmol) for 16 h at 100° in a sealed tube and shown to yield a mixture of compounds (1)—(4) (Table 1). Hydrocarbons, vinylcyclohexene, octa-1,3,7-triene, and cyclo-octadiene, in varying amounts and ratios were also formed. The stereochemistry of the double bond of all adducts was assigned as *trans* on the basis of strong absorption in the 970 cm^{-1} region of the i.r. spectrum and the lack of absorption at 650—700 cm^{-1} which sets an upper limit of the *cis*-isomer at *ca.* 5%. The n.m.r. data for the morpholine–diene adducts (Table 2) were typical for all amine adducts.

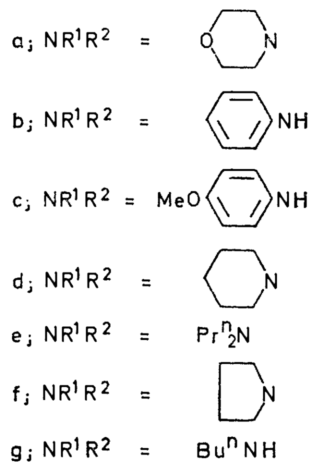
TABLE 1

Reactions of amines with buta-1,3-diene catalysed by nickel acetylacetonate and di-isopropoxyphenylphosphine at 100° [a]

Amine	Reaction (%)	Products (%) (1)	(2)	(3)	(4)
Morpholine [b]	96	15	32	2	51
Piperidine	92	34	39	2	25
Pyrrolidine	96	56	17	2	37
Di-n-propylamine	28	20	55	0	25
n-Butylamine [b]	31	100		Trace	
Aniline [b]	37	56	15	8	21
p-Anisidine [b,c]	64	63	22	1	4

[a] In all cases, $Ni(acac)_2$ (1 mmol), $PhP(OPr^i)_2$ (1·1 mmol), amine (50 mmol), and butadiene (150 mmol), 16 h. [b] Sodium borohydride (0·4 mmol) added. [c] Also formed, dialkylated product (10%).





Reactions of other 1,3-dienes have been studied. With morpholine and isoprene under similar conditions, but with the addition of a small amount of sodium borohydride (0·4 mmol), a 47% yield of a mixture of (5) (10%), (6) (14%), (7) (54%), (8) (17%), and (9) (17%) was obtained. The unambiguous assignment of (9) was based on the occurrence

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[5] R. Baker, D. E. Halliday, and T. N. Smith, *Chem. Comm.*, 1971, 1583.

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TABLE 2

N.m.r. data (τ values) from reaction of 1,3-dienes with morpholine

Adduct	Vinylic	Terminal olefinic	α to oxygen	Allylic and α to nitrogen	α to nitrogen	Allylic	Geminal	Methyl
(1)	4·00—4·50 (1H, m)	4·80—5·20 (2H, m)	6·38 (4H, m)	7·13 (1H, m)	7·54 (4H, m)			8·83 (3H, d, *J* 6 Hz)
(2)	4·50 (2H, m)		6·40 (4H, m)	7·15 (2H, d, *J* 4 Hz)	7·55 (4H, m)			8·30 (3H, d, *J* 4 Hz)
(3)	3·95—4·60 (2H, m)	4·75—5·20 (4H, m)	6·42 (4H, m)	7·28 (1H, m)	7·58 (4H, m)	7·95 (2H, m)	8·50 (4H, m)	
(4)	4·00—4·60 (3H, m)	4·80—5·20 (2H, m)	6·43 (4H, m)	7·14 (2H, d, *J* 4 Hz)	7·68 (4H, m)	8·00 (4H, m)	8·50 (2H, m)	
(5)		5·20 (2H, m)	6·38 (4H, m)	7·30 (1H, m)	7·60 (4H, m)			8·25 (3H, m), 8·80 (3H, d, *J* 6 Hz)
(6)	4·00—4·50 (1H, m)	4·80—5·20 (2H, m)	6·34 (4H, m)		7·46 (4H, m)			8·80 (6H, s)
(7)	4·40—4·80 (1H, m)		6·33 (4H, m)	7·13 (2H, s)	7·63 (4H, m)			8·24 (6H, m)
(8)	4·60—4·90 (1H, m)		6·38 (4H, m)	7·10 (2H, d, *J* 8 Hz)	7·62 (4H, m)			8·29 (6H, s)
(9)	4·40—4·80 (1H, m)	5·00—5·30 (2H, m)	6·36 (4H, m)	7·17 (2H, s)	7·67 (4H, m)	7·98 (4H, m)	8·50 (2H, m)	8·28 (6H, d, *J* 4 Hz)
(10)	4·30—4·65 (2H, m)		6·35 (4H, m)	7·15 (1, m)	7·52 (4H, m)			8·19 (3H, d, *J* 4 Hz) 8·80 (3H, d, *J* 6 Hz)
(11)	4·30—4·60 (2H, m)		6·36 (4H, m)	7·08 (2H, d, *J* 4 Hz)	7·62 (4H, m)	7·95 (2H, m)		8·92 (3H, d, *J* 7 Hz)

TABLE 3

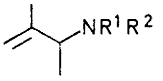
Reactions of amines and butadiene catalysed by nickel salts and phosphines at 100° [a]

						Products (%)			
Amine	Ni(salt)$_2$	Phosphine	Solvent	Time (h)	Reaction (%)	(1)	(2)	(3)	(4)
Morpholine	NiBr$_2$	P(OMe)$_3$ [b]	EtOH	1	30	46	32	2	20
	NiBr$_2$	P(OEt)$_3$	EtOH	1	27	49	38	1	12
	NiBr$_2$	PhP(OMe)$_2$	EtOH	1	18	36	64	Trace	
	NiBr$_2$	PhP(OEt)$_2$	EtOH	1	59	44	39	2	15
	NiBr$_2$	PhP(OPr^i)$_2$	EtOH	1	96	31	59	0·5	9·5
	NiBr$_2$		*	1	98	29	36	2	33
	NiBr$_2$		Pr^{i}OH	1	93	23	46	2	29
	NiBr$_2$		Benzene	1	95	33	28	2	37
	NiBr$_2$		HCONMe$_2$	1	100	38	45	2	15
	NiBr$_2$		Et$_2$O	1	88	32	31	3	35
	NiCl$_2$		EtOH	1	97	31	64	0	5
	Ni(acetate)$_2$		EtOH	1	85	23	19	3	55
	Ni(acetate)$_2$		*	1	70	23	11	11	54
	Ni(hexoate)$_2$		EtOH	1	82	19	16	6	59
	Ni(laurate)$_2$		EtOH	1	84	18	26	2	54
	Ni(acac)$_2$ [c]		EtOH	1	Trace				
	Ni(acac)$_2$ [c]		EtOH	16	95	25	18	1	56
	NiBr$_2$		*	$\frac{1}{2}$	79	33	32	2	33
	NiBr$_2$		*	5	100	22	35	2	41
	NiBr$_2$		*	16	100	19	44	1	36
	NiBr$_2$		*	24	100	18	47	1	34
	NiBr$_2$		*	1 [d]	91	42	23	2	33
	NiBr$_2$		*	1 [e]	23	42	24	1	33
n-Butylamine	NiBr$_2$		EtOH	1	100 [f]	20	14	0	9
	Ni(acetate)$_2$		EtOH	1	Trace				
	Ni(acetate)$_2$		EtOH	16	96 [g]	24	11	0	10
	Ni(acac)$_2$ [c]		EtOH	1	64	58	42	Trace	
Pyrrolidine	NiBr$_2$		EtOH	1	86	58	26	3	13
Aniline	NiBr$_2$		*	16	45	38	62	Trace	
Di-n-propylamine	NiBr$_2$		EtOH	1	47	19	48	0	33

* No solvent.

[a] In all cases Ni(salt)$_2$ (1 mmol), phosphine (1·1 mmol), solvent (5 ml), amine (50 mmol), and butadiene (150 mmol). [b] Under the same conditions P(OPh)$_3$ gave trace reaction and PPh$_3$ no reaction. [c] Sodium borohydride (0·4 mmol) added. [d] 75°. [e] 50°. [f] Also formed, dialkylated products (12) (5%), (13) (15%), (14) (5%), (15) (23%), (16) (9%). [g] Also formed, dialkylated products (12) (5%), (13) (19%), 14 (4%), (15) (13%), (16) (13%).

of a singlet for the allylic group α to the nitrogen protons which confirms the tail–tail mode of dimerisation of isoprene. No 2 : 1 adduct was obtained in reaction of morpholine and *trans*-piperylene which gave an 80% conversion into a 1 : 1 mixture of adducts (10) and (11).



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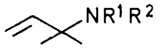

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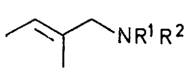

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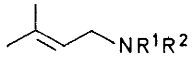

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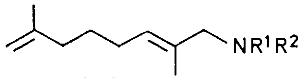

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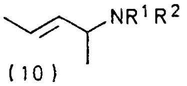

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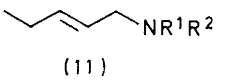

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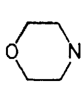
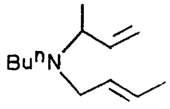


A standard procedure was employed to study the effect of a number of parameters on the conversions and product ratios (Table 3). In general, it was found that the greatest reaction was obtained using anhydrous nickel bromide and di-isopropoxyphenylphosphine as catalyst with ethanol as solvent. This catalyst system gave the series of dialkylated products (12)—(16) together with (1), (2), and (4) from reaction of butadiene and n-butylamine.



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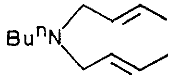

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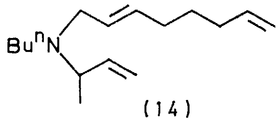

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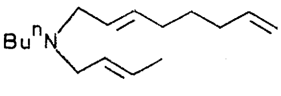

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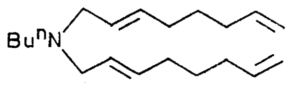

(16)

DISCUSSION

The nickel catalyst is suggested to be a nickel(0) complex. Gray *et al.*[7] have established that phenyldiethoxy- and phenyldimethoxy-phosphines form tetrakis(organophosphorus)nickel(0) species from nickel halides in refluxing alcohol solvent and trimethyl and triethyl phosphite also reduce nickel halides to nickel(0) complexes in the presence of a tertiary amine and water.[8] The extent to which the reducing properties of di-isopropoxyphenylphosphine are affected by the reaction medium is illustrated in the preparation of tetrakis(di-isopropoxyphenylphosphine)nickel. Di-isopropoxyphenylphosphine (0·5 equiv.) and nickel bromide (0·1 equiv.) in refluxing propanol gave a red solution from which bis(di-isopropoxyphenylphosphine)nickel dibromide crystallised. However, when an excess of triethylamine was added, tetrakis(di-isopropoxyphenylphosphine)nickel readily precipitated and it is clear that the presence of amine is assisting the reduction process.

Butenyl and octadienyl adducts are thought to arise from the π-allylnickel (17) and bis-π-allylnickel complexes (18) as suggested for the active methylene (and phenol)-1,3-diene nickel catalysed reactions (Scheme).[9,10] Whilst formation of the butenyl adduct by direct nucleophilic attack on the co-ordinated ligand cannot be excluded, the ready formation of π-allylnickel complexes in the presence of nickel(0) complexes [11,12] and the lack of reactivity of a nickel π-complex towards nucleophiles is indicative of the intervention of (17).

Reaction of morpholine, butadiene, and ethanol with the $\mathrm{NiL_4}$ species $\mathrm{Ni[PhP(OEt)_2]_4}$ or $\mathrm{Ni[PhP(OPr^i)_2]_4}$ for 1 h at 100° revealed only trace reaction and 96% conversion respectively {total conversion was found after 16 h at 100° with $\mathrm{Ni[PhP(OEt)_2]_4}$}. From a consideration of the steric properties of the phosphines, the dissociation of the $\mathrm{NiL_4}$ complexes into the catalytically active forms $\mathrm{NiL_3}$ or transitory $\mathrm{NiL_2}$ should increase with size of the phosphine.[13] At room temperature, no evidence of dissociation was found with $\mathrm{Ni[PhP(OEt)_2]_4}$ and $\mathrm{Ni[PhP(OMe)_2]_4}$.[7] The conditions employed for reactions with $\mathrm{NiBr_2}$ and dialkoxyphenylphosphine are very similar to those used in the preparation of $\mathrm{NiL_4}$ complexes and this complex, or a dissociated species, must be formed. The ease of dissociation of $\mathrm{NiL_4}$ is greater for $\mathrm{L = PhP(OPr^i)_2}$ than for $\mathrm{PhP(OEt)_2}$ and this would explain the reactivity order observed with preformed and *in situ* reduced nickel complexes. The earlier suggestion by Rose that the special reactivity of di-isopropoxyphenylphosphine is due to interaction between the metal and the secondary hydrogen of the alkoxy-group [14] does not appear necessary to explain the observation.

Control experiments showed that the branched butenyl–morpholine adduct (1a) is totally isomerised to the linear butenyl adduct (2a) after 4 h at 100° with nickel acetylacetonate and di-isopropoxyphenylphosphine (catalyst–substrate ratio 1 : 13). A kinetic preference is therefore shown for formation of 1-methylprop-2-enylamines over but-2-enylamines. The [1,3]

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[7] A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, 1969, **3**, 8.

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[12] A. C. L. Su and J. W. Collette, *J. Organometallic Chem.*, 1972, **36**, 177.

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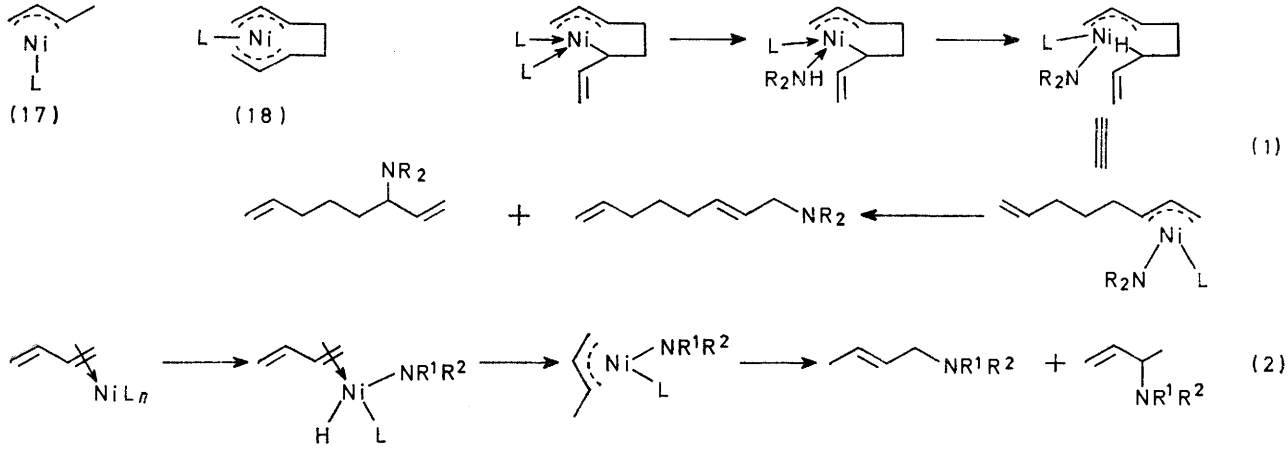
[14] D. Rose, *Tetrahedron Letters*, 1972, 4197.

isomerisation of the amino-group is best explained by reversible formation of the π-allylnickel complex which yields the thermodynamically more stable linear amine adduct on further reaction in a similar manner to that reported for butadiene–phenol in the presence of nickel(0) complexes.[9] No conversion was found from butenyl into octadienyl product, or the reverse, in any experiments.

Factors Determining Butenyl and Octadienyl Adducts.—No clear trend is apparent in the competition between butenyl and octadienyl adduct formation with different amines and morpholine is the only reagent which yields less of the former in a variety of the conditions.

Some control of the amount of butenyl adduct can be achieved by a change in the ratio of dialkoxyphenylphosphine–nickel salt concentration. In the presence of di-isopropoxyphenylphosphine and nickel bromide, reaction of butadiene and morpholine gives a butenyl–octadienyl ratio of 68 : 32 when the P–Ni ratio is 1·1 : 1 and this changes to 92 : 8 when the ratio is 3 : 1.



Scheme

Addition of ethanol (1 ml) to morpholine in the presence of the complex $[PhP(OPr^i)_2]NiBr_2$ changes the butenyl–octadienyl ratio from 42 : 58 to 74 : 26. This could be due to formation of a protonated nickel species[15] which would favour formation of a π-allylnickel intermediate thus favouring formation of the butenyl adduct. In the presence of nickel halides the use of co-ordinating solvents such as ethanol and dimethylformamide results in formation of a greater proportion of butenyl adduct. The availability of a proton and enhanced formation of a π-allylnickel complex could be the determining factor in the case of ethanol as described above but, in general, competition of solvent, diene, and amine around the central metal atom would make 2 : 1 adduct formation less favourable.

In general, two features of the reactions are apparent when the nickel salt is changed. A greater proportion of butenyl adduct is found when nickel halide is used and the order of reactivity of the catalyst system is nickel halide > nickel (aliphatic acid salts) ≫ nickel acetylacetonate. This reactivity order may partially reflect the ease of reduction of these salts.[16] The relative lack of reaction of nickel acetylacetonate has previously been attributed to its known complexing properties with amines. Since a similar product distribution is found when either preformed $Ni[PhP(OPr^i)_2]_4$ or when nickel halide is reduced *in situ* with the di-isopropoxyphenylphosphine in ethanol, involvement of a common nickel(0) complex is indicated. However, a different product distribution is found when other nickel salts are employed and it is possible that a complex $Ni[PhP(OPr^i)_2]_nL_m$ is the active species; a ligand L might be identified as the anion from the nickel salt.

Butenyl formation can also be favoured by maintaining only a low concentration of butadiene. Thus, when butadiene gas (60 ml min^{-1}) was passed into a solution of nickel bromide (1 mmol) and di-isopropoxyphenylphosphine (1·1 mmol) at 80° there was an immediate reaction to yield exclusively butenyl products. Morpholine (50 mmol) was totally converted in 20 min into a mixture of (1a) and (2a) which completely isomerised to (2a) (98%) after a further 20 min.

Substituents in the 1,3-diene markedly reduce the amount of octadienyl products. Thus with isoprene only 17% of 2 : 1 adducts are formed and piperylene yields exclusively 1 : 1 adducts with morpholine.

A number of changes can be made in the standard conditions which increases the amount of octadienyl adduct formed between butadiene and morpholine. Thus, increasing the diene–amine ratio to 9 : 1 in the presence of nickel acetylacetonate and di-isopropoxyphenylphosphine gives 87% conversion in 14 h at 100° into (1a) (13%), (2a) (21%), (3a) (2%), and (4a) (64%). A similar conversion and product mixture is also found in benzene when the diene–amine ratio is 3 : 1.

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[15] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

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The most favourable octadienyl formation was found, however, with preformed $Ni[(PhO)_3P]_4$ which in ethanol and with a catalyst–substrate ratio of 1 : 250 gave a 71% conversion into (1a) (9%), (2a) (5%), (3a) (7%), and (4a) (79%) in 16 h at 100°. With $Ni[PhP(OPr^i)_2]_4$, however, a 94% conversion into (1a) (30%), (2a) (59%), (3a) (1%), and (4a) (10%) was obtained. An explanation is that this difference is probably caused by the greater tendency of $Ni[(PhO)_3P]_4$ to dissociate into a $Ni[(PhO)_3P]_2$ complex due to the large size of associated ligands. A good yield of an octadienyl–morpholine adduct has also been reported by Heimbach in the presence of a nickel–triethyl phosphite catalyst.[17] In this case the temperature was shown to be important and the product had a different position for one double bond compared to the present work. Isomerisation of the product under their conditions is a possibility.

Role of Sodium Borohydride.—The use of sodium borohydride, employed in earlier reported reactions,[5,14] has been found to be very specific. In reactions catalysed by nickel acetylacetonate in the absence of solvent, its use has been shown to be essential for morpholine, and very beneficial for reactions involving n-butylamine and aniline. In the absence of borohydride, n-butylamine and aniline are converted in 7 and 18% yield respectively; this increases to 31 and 38% when sodium borohydride (0·4 mmol) is added (the product ratio is unaffected), and only a trace reaction of morpholine and butadiene is found if sodium borohydride is excluded. Nickel acetylacetonate forms many stable amine salts,[18] their stability being one of degree, with the morpholine complex being apparently particularly stable to reduction by phosphine. The complex $(morpholine)_2Ni(acac)_2$ was prepared[19] and found not to catalyse the reaction in the absence of solvent or $NaBH_4$. However on addition of sodium borohydride reaction proceeded smoothly in 79% conversion into the products (1a)—(4a). The same complex in ethanol with no borohydride also catalyses the morpholine–butadiene reaction in 96% conversion into (1a) (28%), (2a) (27%), (3a) (3%), and (4a) (42%). Nickel acetylacetonate in ethanol catalyses the same reaction in 94% conversion into (1a) (25%), (2a) (20%), (3a) (3%), and (4a) (52%), in the absence of borohydride. In all reactions a 1 : 1·1 ratio of nickel salt to di-isopropoxyphenylphosphine was employed. It is evident that sodium borohydride and ethanol prevent formation or break down the amine complex. When sodium borohydride and ethanol are used together with nickel acetylacetonate, the conversion of n-butylamine improves to 61% into a mixture of (1g) (58%) and (2g) (42%) after 16 h at 100°. After addition of small amounts of sodium borohydride, the addition of larger quantities does not continue to improve the reaction and only a substantial increase in hydrocarbon is found. Only when a phosphine, such as triphenylphosphine, is used does the reducing property of sodium borohydride become important. Although a complex mixture of products, with only 5% conversion of morpholine, is found when nickel halide, butadiene, and ethanol are treated according to the standard procedure with triphenylphosphine, when a mixture of nickel chloride, sodium borohydride, triphenylphosphine, and butadiene is treated with morpholine and butadiene at room temperature and atmospheric pressure, 85% conversion is found into a mixture containing 92% of the octadienyl adduct.[20] The borohydride assumes the role of reduction to form the active catalyst species. A similar catalyst was reported[21] for the formation of hydro-oligomers of butadiene, but no hydrotelomers were formed in the above reaction.

EXPERIMENTAL

Reactions were performed in sealed Carius tubes which were placed in constant temperature oil-baths. Reagent amines were distilled before use and solvents, where applicable, were purged with nitrogen before use. Butadiene was passed over potassium hydroxide pellets to remove the inhibitor and moisture and distilled into the reaction vessel on a vacuum line. Isoprene and *trans*-piperylene were purified by distillation.

Di-isopropoxyphenyl-, diethoxyphenyl-, and dimethoxyphenyl-phosphine were prepared according to Rabinowitz and Pellon[22] and purified by distillation under reduced pressure, spectral data being consistent with those of the authentic phosphines. Triphenyl, triethyl, and trimethyl phosphites were used as supplied without further purification. Triphenylphosphine was recrystallised from benzene–light petroleum (b.p. 100—120°).

Anhydrous nickel acetylacetonate, nickel bromide, nickel chloride, and nickel acetate were obtained from their hydrates by heating at 80° and 1 mmHg for 16 h. Nickel hexanoate and nickel laurate were prepared from nickel sulphate and hexanoic and lauric acid respectively.

Tetrakis(diethoxyphenylphosphine)nickel was prepared by the method of Gray *et al.*[7] (Found: C, 55·8; H, 7·02; P, 15·1. $C_{40}H_{60}NiO_8P_4$ requires C, 56·5; H, 7·11; P, 14·6%).

Tetrakis(di-isopropoxyphenylphosphine)nickel was prepared by reaction of di-isopropoxyphenylphosphine (50 mmol), anhydrous nickel chloride (10 mmol), and triethylamine (50 mmol) in refluxing propan-2-ol for 3 h under nitrogen. The extremely air sensitive yellow solid which crystallised from the mixture was washed several times with propan-2-ol and dried under vacuum (Found: C, 60·9; H, 7·7; P, 12·4. $C_{48}H_{76}NiO_8P_4$ requires C, 61·6; H, 8·1; P, 12·9%).

Bis(di-isopropoxyphenylphosphine)nickel dibromide was prepared by reaction of di-isopropoxyphenylphosphine (50 mmol) and anhydrous nickel bromide (10 mmol) in refluxing propan-2-ol for 3 h under nitrogen. On slow cooling, a red crystalline compound was deposited which was washed with propan-2-ol and dried under vacuum (Found: C, 42·2; H, 5·5; P, 9·7. $C_{24}H_{38}Br_2NiO_4P_4$ requires C, 42·9; H, 5·65; P, 9·25%). An ethanol solution

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of the solid on treatment with silver nitrate solution gave a cream precipitate confirming the presence of bromide.

Tetrakis(triphenyl phosphite)nickel was prepared by the method of McLaughlin,[23] and bis(morpholine)nickel acetylacetonate by the method of Marcotrigiano *et al.*[19]

A Pye 104 chromatograph was employed for all g.l.c. analyses (nitrogen carrier gas through 5 ft × 0·25 in glass column; 10% E 301) and a Pye 105 chromatograph for all preparative g.l.c. (nitrogen carrier gas through 15 ft × 0·375 in glass column, 25% E 301). Height × width at half-height was used to measure peak areas and yields were expressed in terms of percentage conversion of amine. N.m.r. spectra were obtained with a Perkin-Elmer R12 instrument using tetramethylsilane as internal standard and carbon tetrachloride or deuteriochloroform as solvent.

General Procedure.—A mixture of anhydrous nickel bromide (1·0 mmol), di-isopropoxyphenylphosphine (1·1 mmol), morpholine (50 mmol), and butadiene (150 mmol) was heated for 1 h at 100° giving a 98% conversion into (1a) (29%), (2a) (36%), (3a) (2%), (4a) (33%), together with a small amount of octa-1,3,7-triene and 4-vinylcyclohexene. Fractional distillation gave a first fraction containing hydrocarbons and morpholine (0·28 g), b.p. 115—130°. Further distillation gave a fraction containing a mixture of (1a) and (2a) (3·8 g), b.p. 60—75° at 20 mmHg, a fraction containing (2a), (3a), and mainly (4a) (1·42 g), b.p. 75—105° at 20 mmHg, a fraction of almost exclusively (4a) (1·21 g), b.p. 110—120° at 20 mmHg, and a final fraction (0·6 g), b.p. 80—140° at 1 mmHg containing (4a) and di-isopropoxyphenylphosphine oxide. Complete separation was achieved by preparative g.l.c.

This general procedure was used for the series of experiments (Table 3) and, where applicable, 5 ml of solvent was added. After fractional distillation, final separation was by preparative g.l.c. The adducts (1)—(8), (10), and (11) have been previously characterised.[1,3]

Reaction of Butadiene with Other Amines.—*Aniline.* Reaction of aniline (50 mmol) with butadiene in the presence of nickel acetylacetonate (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), and sodium borohydride (0·4 mmol) at 100° for 16 h gave a 37% conversion into (1b) (56%), (2b) (15%), (3b) (8%), and (4b) (21%); 13% of the mixture consisted of octa-1,3,7-triene, 4-vinylcyclohexene, and cyclo-octa-1,5-diene in the ratio 1 : 11 : 10. Fractional distillation did not achieve a complete separation and the early fractions comprised mixtures of hydrocarbons, aniline, and butenyl derivatives. A mixture of the butenyl adducts (1b) and (2b) and a further fraction containing mixtures of butenyl and octadienyl derivatives and phosphine oxide was obtained.

p-*Anisidine.* *p*-Anisidine (50 mmol) gave a 64% conversion into (1c) (63%), (2c) (22%), (3c) (1%), and (4c) (4%) and a dialkylated product (10%) with a linear C_4 and linear C_8 chain upon treatment with nickel acetylacetonate (1 mmol), di-isopropoxyphenylphosphine (1 mmol), and sodium borohydride (0·3 mmol). Distillation afforded three fractions, one containing octa-1,3,7-triene, 4-vinylcyclohexene, cyclo-octa-1,5-diene, anisidine, and butenyl derivatives, a second in which butenyl amines predominated, and a third containing mixtures of all five alkylated amines.

Piperidine. The reaction of nickel acetylacetonate (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), piperidine (50 mmol), and butadiene (150 mmol) gave a 92% conversion into (1d) (34%), (2d) (39%), (3d) (2%), and (4d) (25%). Distillation gave fractions consisting of piperidine, 4-vinylcyclohexene, and cyclo-octa-1,5-diene, (1d) and (2d), and finally one consisting of predominantly (4d).

Di-n-propylamine. The reaction of nickel bromide (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), di-n-propylamine (50 mmol), and butadiene (150 mmol) in ethanol (5 ml) gave a 47% conversion into (1e) (19%), (2e) (48%), and (4e) (33%) after 1 h at 100°. Distillation gave a crude separation of fractions of ethanol and di-n-propylamine, a mixture of (1e) and (2e), and a fraction rich in (4e).

Pyrrolidine. The reaction of nickel bromide (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), pyrrolidine (50 mmol), and butadiene (150 mmol) gave a 70% conversion of amine after 1 h at 100° into (1f) (23%), (2f) (11%), (3f) (11%), and (4f) (54%). Distillation gave fractions containing mainly pyrrolidine and a small amount of 4-vinylcyclohexene, (1f) and (2f), a mixture of (1f)—(4f), (3f) and (4f), and finally di-isopropoxyphenylphosphine and (4f).

n-Butylamine. The reaction of nickel acetate (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), n-butylamine (50 mmol), and butadiene (150 mmol) in ethanol (5 ml) gave a 100% conversion of amine into a mixture of (1g) (24%), (2g) (11%), (4g) (10%), (12) (5%), (13) (19%), (14) (4%), (15) (13%), and (16) (13%). Fractional distillation gave a crude separation into (1g) and (2g), a mixture of (1g), (2g), (4g), (12), and (13), a mixture of (4g), (12)—(15), (14) and (15), and a final fraction rich in (16): compound (12) τ (CCl_4) 3·9—4·65 (3H, m), 4·9—5·2 (2H, m), 6·8 (1H, m), 7·1 (2H, d), 7·7 (2H, t, *J* 6 Hz), 8·55—8·8 (4H, m), 8·9 (3H, d, *J* 7 Hz), and 9·1 (3H, t, *J* 6 Hz), *m/e* 181 (0·5%), 138 (16), 84 (18), 55 (100), and 41 (21), $\nu_{max.}$ 3030, 2940, 1455, 1370, 970, and 920 cm^{-1}; compound (13) τ (CCl_4) 4·57 (4H, m), 7·13 (4H, m), 7·68 (2H, t, *J* 6 Hz), 8·6—8·9 (4H, m), 8·35 (6H, 2 × d, *J* 4 Hz), and 9·1 (3H, t, *J* 6 Hz), *m/e* 181, 166, 138, 84, 55 (100%), 42, and 41, $\nu_{max.}$ 3030, 2940, 1465, 1395, and 970 cm^{-1}; compound (14) τ (CCl_4) 3·9—4·65 (4H, m), 4·8—5·2 (4H, m), 6·8 (1H, m), 7·12 (2H, d, *J* 4 Hz), 7·67 (2H, t, *J* 6 Hz), 7·8—8·15 (4H, m), 8·35—8·9 (6H, m), 8·92 (3H, d, *J* 7 Hz), and 9·1 (3H, t, *J* 6 Hz), *m/e* 235 (2%), 192 (13), 166 (100), 107 (18), 55 (47), and 41 (21); compound (15) τ (CCl_4) 3·95—4·65 (5H, m), 4·9—5·22 (2H, m), 7·07—7·17 (4H, m), 7·67 (2H, t, *J* 6 Hz), 7·8—8·15 (4H, m), 8·35—8·9 (6H, m), 8·35 (3H, d, *J* 4 Hz), and 9·1 (3H, t, *J* 6 Hz), *m/e* 235 (2%), 192 (100), 67 (40), 55 (64), and 41 (24), $\nu_{max.}$ 3030, 2940, 1640, 1465, 1453, 1267, 990, 950, and 920 cm^{-1}; compound (16) τ (CCl_4) 3·9—4·65 (6H, m), 4·9—5·2 (4H, m), 7·07 (4H, d, *J* 4 Hz), 7·6—8·1 (10H, m), 8·3—8·8 (8H, m), and 9·1 (3H, t, *J* 6 Hz), *m/e* 289 (4%), 244 (100), 198 (37), 67 (78), 55 (67), and 41 (45), $\nu_{max.}$ 3030, 2940, 1640, 1468, 1455, 975, and 920 cm^{-1}.

Reaction of Morpholine with Other Dienes.—*Isoprene.* The reaction of morpholine (50 mmol) and isoprene (150 mmol) in the presence of nickel acetylacetonate (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), and sodium borohydride (0·4 mmol) gave a 47% conversion of amine into (5) (10%), (6) (14%), (7) (54%), (8) (5%), and (9) (17%); 12% of the reaction mixture consisted of four hydrocarbons, each of which had a mass ion of 136. The products were separated by fraction distillation and after a forerun of unchanged isoprene, morpholine, hydrocarbons, and some C_5 adducts, a mixture of the adducts (5)—(8) was obtained. Pure (9), b.p. 100—110° at 1 mmHg, $\nu_{max.}$ 2950, 1660, 1465, 1360, 1260, 890, 875, and 790 cm^{-1}, *m/e* 223 (*M*$^+$, 32%), 100 (100), 86 (64), 82 (36), 81 (45), 67 (32), 56 (50), 55 (41), and 41 (73).

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trans-*Piperylene*. Reaction of morpholine (50 mmol) with *trans*-piperylene (150 mmol) in the presence of nickel acetylacetonate (1 mmol), di-isopropoxyphenylphosphine (1·1 mmol), and sodium borohydride (0·4 mmol) gave an 80% conversion of amine into (10) (50%) and (11) (50%). No hydrocarbon was observed. A crude separation was achieved by fractional distillation.

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