Reactions of Active Methylene Compounds with 1,3-Dienes catalysed by Nickel Complexes

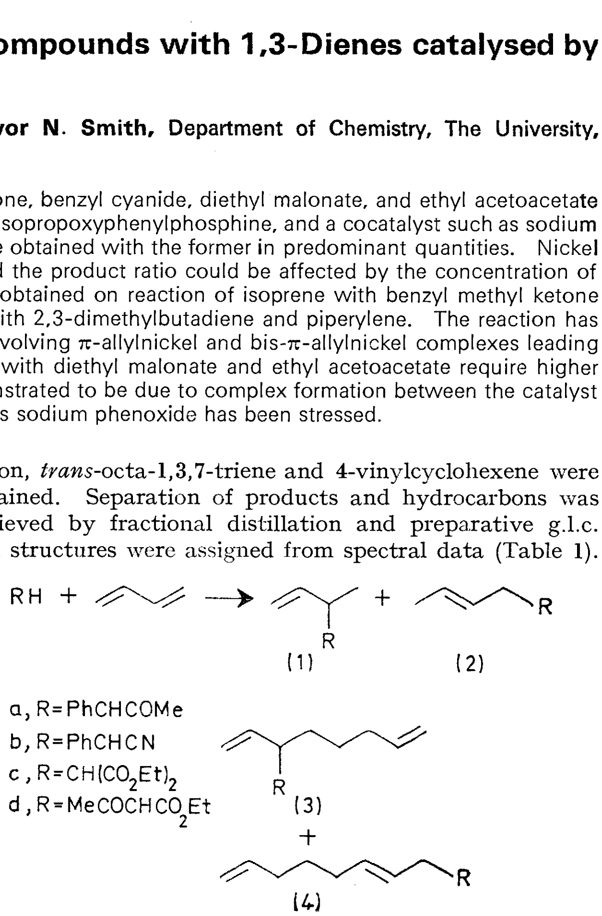
By **Raymond Baker,*** **Alan H. Cook,** and **Trevor N. Smith,** Department of Chemistry, The University, Southampton SO9 5NH

Reactions of buta-1,3-diene with benzyl methyl ketone, benzyl cyanide, diethyl malonate, and ethyl acetoacetate have been studied in the presence of nickel salts, di-isopropoxyphenylphosphine, and a cocatalyst such as sodium phenoxide. Mixtures of 2 : 1 and 1 : 1 adducts were obtained with the former in predominant quantities. Nickel halides provided the most active catalyst system and the product ratio could be affected by the concentration of reagents and phosphine. Mainly 1 : 1 adduct was obtained on reaction of isoprene with benzyl methyl ketone and exclusive formation of this adduct was found with 2,3-dimethylbutadiene and piperylene. The reaction has been suggested to occur by competing processes involving π-allylnickel and bis-π-allylnickel complexes leading to 1 : 1 and 2 : 1 adducts, respectively. Reactions with diethyl malonate and ethyl acetoacetate require higher amounts of the nickel system which has been demonstrated to be due to complex formation between the catalyst and reagents. The importance of cocatalysts such as sodium phenoxide has been stressed.

REACTIONS of active hydrogen compounds with buta-1,3-diene have been reported with catalysis by both nickel and palladium complexes. Palladium(0) complexes have been shown to catalyse the reaction of butadiene with alcohols,[1,2] water,[3] amines,[1,2,4] carboxylic acids,[1,2,5] and active methylene and methyne compounds.[4,6] Telomerisation of methanol with butadiene, catalysed by a nickel complex gave a mixture of butenyl and octadienyl ethers.[7] With ethanol, although a more efficient formation of octadienyl ethers was found, a lower conversion of butadiene was obtained and no reaction occurred with isopropyl or t-butyl alcohols. In the present paper, we report reactions of 1,3-dienes with active methylene compounds catalysed by a system comprising a nickel(II) salt, di-isopropoxyphenylphosphine, and a cocatalyst such as sodium phenoxide.[8] The reactions provide a synthetic route into a number of long chain alicyclic derivatives some of which could provide intermediates for terpenoid derivatives.

RESULTS

Treatment of benzyl methyl ketone with a three molar excess of butadiene in the presence of a catalyst system comprising nickel acetylacetonate, di-isopropoxyphenylphosphine, and sodium phenoxide in ethanol gave a 90% conversion into a mixture of four adducts after 16 h at 75°. Substitution of the diene occurred only at the benzylic position yielding butenyl and octadienyl adducts (1a) (15%), (2a) (19%), (3a) (4%), and (4a) (62%). In addition, *trans*-octa-1,3,7-triene and 4-vinylcyclohexene were obtained. Separation of products and hydrocarbons was achieved by fractional distillation and preparative g.l.c. and structures were assigned from spectral data (Table 1).



Evidence for two diastereoisomers was found in the n.m.r. of (1a) in that two doublets appeared at τ 9·00 and 9·30 attributable to the methyl group being in different environments. Molecular models give an indication of the different degree of shielding provided by the phenyl on the methyl group. The presence of methyl group and olefinic protons at τ 4·50 and 5·20 in the ratio of 1 : 2 confirm the terminal position of the double bond in the butenyl adduct (1a). Methyl and olefinic protons at τ 8·45 and 4·50 confirm the presence of an internal double bond in the structure of (2a). *trans*-Stereochemistry was assigned to the double bond on the evidence of a strong peak at 960—970 cm^{-1} in the i.r. spectrum.

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

[2] E. J. Smutny, *J. Amer. Chem. Soc.*, 1967, **89**, 6793.

[3] K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem. Comm.*, 1971, 330.

[4] K. Takahashi, A. Miyake, and G. Hata, *Bull. Chem. Soc. Japan*, 1972, **45**, 1183.

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

[6] G. Hata, K. Takahashi, and A. Miyake, *J. Org. Chem.*, 1971, **36**, 2116.

[7] T. C. Shields and W. E. Walker, *Chem. Comm.*, 1971, 193.

[8] R. Baker, D. E. Halliday, and T. N. Smith, *J. Organometallic Chem.*, 1972, **85**, C61.

TABLE 1

N.m.r. data (τ values) for products from reaction of 1,3-dienes and benzyl methyl ketone

Compound	Aromatic	Vinylic	Terminal olefinic	Benzylic	Allylic α-benzylic	Allylic	Acetyl *	Methyl *	Methylene
(1)	2·90 (5H, s)	4·10—4·80 (1H, m)	4·80—5·40 (2H, m)	6·65 (d, *J* 10 Hz)	6·90—7·30 (1H, m)		8·05 (s)	9·00, 9·30 (d, *J* 7 Hz)	
(2)	2·85 (5H, s)	4·20—4·90 (2H, m)		6·50 (t, *J* 7 Hz)	7·10—7·80 (2H, m)		8·10 (s)	8·45 (d, *J* 4 Hz)	
(3)	2·80 (5H, s)	4·10—4·70 (2H, m)	4·85—5·30 (4H, m)	6·55 (1H, d, *J* 10 Hz)	7·10—7·50 (1H, m)	7·90—8·10 (2H, m)	8·00 (s)		8·60 (4H, m)
(4)	2·80 (5H, s)	3·90—4·85 (3H, m)	4·90—5·30 (2H, m)	6·30 (1H, t, *J* 8 Hz)	7·40 (2H, m)	8·00—8·20 (4H, m)	8·05 (s)		8·60 (2H, m)
(5)	2·80, 2·85 (5H, s)		5·25—5·55 (2H, m)	6·35; 6·45 (1H, d, *J* 11 Hz)	6·90—7·35 (1H, m)		8·00, 8·05 (s)	8·25, 8·60 (s), 8·95, 9·30 (d, *J* 7 Hz)	
(6)	2·80 (5H, s)	4·90 (1H, m)		6·30 (1H, t, *J* 7 Hz)	7·30—7·70 (2H, m)		8·05 (s)	8·50 (s), 8·55 (d, *J* 7 Hz)	
(7)	2·80 (5H, s)	4·70—5·05 (2H, m)	5·10—5·50 (2H, m)	6·30 (1H, t, *J* 7 Hz)	7·55 (2H, m) (3H, m)	7·90—8·30	8·05 (s)	8·50 (s), 9·10 (d, *J* 7 Hz)	8·40 (2H, m)
(8)	2·80 (5H, s)	5·00 (1H, t, *J* 7 Hz)	5·40 (2H, m)	6·30 (1H, t, *J* 8 Hz)	7·55 (2H, m)	8·10 (4H, m)	8·05 (s)	8·40, 8·50 (6H, s)	8·30 (2H, m)
(9)	2·80 (5H, s)		4·80—5·30 (2H, m)	6·25 (1H, t, *J* 8 Hz)			8·10 (s)	8·40 (s), 8·75 (6H, s)	
(10)	2·80 (5H, s)			6·25 (1H, *J* 8 Hz)	7·35 (2H, m)		8·10 (s)	8·25—8·60 (9H, 3s)	
(12A)	2·80 (5H, m)	4·75—5·00 (2H, m)		6·70 (1H, d, *J* 11 Hz)	7·20 (1H, m)		8·05 (s)	8·60 (d, *J*, 5 Hz), 9·00 (d, *J* 6 Hz)	
(12B)	2·85 (5H, m)	4·50—4·70 (2H, m)		6·60 (1H, *J* 11 Hz)	7·10 (1H, m)		8·10 (s)	8·30 (d, *J* 5 Hz) 9·25 (d, *J* 6 Hz)	
(13)	2·80 (5H, s)	4·50—4·80 (2H, m)		6·40 (1H, t, *J* 7 Hz)	7·40 (2H, m)	8·00 (2H, m)	8·00 (s)	9·00 (t, *J* 7 Hz)	

* 3H except where noted.

TABLE 2

Reaction of buta-1,3-diene and benzyl methyl ketone [a]

Diene–ketone	Phosphine–nickel	Phenoxide–nickel	Temp. (%)	Time (h)	Reaction (%)	C_4 Products (%)		C_8 Products (%)		Hydrocarbon[b] (%)
						(1)	(2)	(3)	(4)	
1 : 1	1·5 : 1	2 : 1	75	16	65	45	44	1	10	
3 : 1	1·5 : 1	2 : 1	75	16	90	15	19	4	62	
10 : 1	1·5 : 1	2 : 1	75	16	26	10	10	5	75	
3 : 1	1·5 : 1	2 : 1	75	0·5	7	12	12	2	74	
3 : 1	1·5 : 1	2 : 1	75	6	34	14	16	5	65	
3 : 1	1·5 : 1	2 : 1	75	12	65	18	22	3	57	
3 : 1	1·5 : 1	2 : 1	75	16	90	15	19	4	62	
3 : 1	1·5 : 1	2 : 1	75	63	88	10	13	5	72	13
3 : 1	1·5 : 1	2 : 1	100	16	68	13	16	4	67	27
3 : 1	0·5 : 1	2 : 1	75	6	10	2	2	7	89	
3 : 1	1 : 1	2 : 1	75	6	51	7	9	5	79	
3 : 1	2 : 1	2 : 1	75	6	61	17	19	4	60	
3 : 1	3 : 1	2 : 1	75	6	75	20	23	3	54	
3 : 1	4 : 1	2 : 1	75	6	66	24	28	2	46	
3 : 1	6 : 1	2 : 1	75	6	55	30	31	3	36	
3 : 1	1·5 : 1	1 : 2	75	6	30	16	18	2	64	
3 : 1	1·5 : 1	1 : 1	75	6	54	15	20	5	60	
3 : 1	1·5 : 1	4 : 1	75	6	90	16	19	3	62	
3 : 1	1·5 : 1	8 : 1	75	6	69	14	15	5	66	

[a] Standard reaction conditions: $PhCH_2COMe$ (0·05 mol), butadiene (0·15 mol), $Ni(acac)_2$ (0·75 mmol), $PhP(Pr^iO)_2$ (1·13 mmol), PhONa (1·4 mmol). [b] No figure is quoted if hydrocarbons produced are <5% of total weight of products.

Olefinic signals at τ 4·40 and 5·10 in the ratio of 1 : 2 and the methylene protons at τ 8·00 and 8·60 confirm the presence of two terminal double bonds and the branched structure (3a). The position of substitution of the benzylic group at C-3 is shown by the clear doublet of the benzylic proton at τ 6·55 and the allylic multiplet at 7·30. The linear structure of (4a) was assigned on the basis of vinylic and terminal olefinic proton signals at τ 4·30 and 5·10, respectively, in the ratio of 3 : 2, and methylene signals at τ 8·10 and 8·60. The position of the internal double bond is β to the benzylic protons, for only in this position can a high field methylene at τ 8·60, corresponding to hydrogens β to both double bonds, be explained. The i.r. spectrum of (4a) shows absorptions at 920 and 1000 cm^{-1} due to a terminal double bond and 980 cm^{-1} indicating the presence of an internal disubstituted double bond which was assigned *trans*-stereochemistry.

A standard procedure was adopted to study the effect of a number of parameters on the conversion, product distribution, and the amount of hydrocarbon produced in the reaction of benzyl methyl ketone and butadiene. These included (*a*) the diene–active methylene compound ratio, (*b*) reaction time, (*c*) temperature, (*d*) amount of sodium phenoxide employed, (*e*) the nickel salt–di-isopropoxyphenylphosphine ratio, and (*f*) the solvent employed (Table 2). Alcoholic solvents were found to be the most suitable and although ethanol was mainly used, comparable results were found in n-butanol or propan-2-ol. Reactions could also be achieved in the absence of solvent but, although the ratios of octadienyl to butenyl products were similar, the reaction rates were slower in the absence of a protic solvent. The use of a strongly co-ordinating solvent such as dimethylformamide gave reduced reaction and a higher proportion of butenyl adducts; this could be the result of competition between the solvent and diene molecules for co-ordination to the catalytic intermediate. No reaction was observed in benzene but a relatively slow reaction could be achieved in tetrahydrofuran at 100°.

TABLE 3

Reactions of buta-1,3-diene and active methylene compounds [a]

Compound	Time (h)	Cocatalyst	Temp. (°C)	Yield (%)	Products (%) (1)	(2)	(3)	(4)
$PhCH_2COMe$	16	PhONa	75	90	15	19	4	62
$PhCH_2COMe$	16	Na_2CO_3	100	57	23	26	3	48
$PhCH_2COMe$	16	$NaBH_4$	75	78	14	13	4	69
$PhCH_2COMe$	16	PhOH	75	85	17	20	4	59
$PhCH_2CN$	16	PhONa	100	30	13	10	13	62
$CH_2(CO_2Et)_2$ *	16	PhONa	100	96	39	35	3	13
$MeCOCH_2CO_2Et$ †	15	PhONa	100	100				16

[a] RH (0·05 mol), butadiene (0·15 mol), $Ni(acac)_2$ (0·75 mmol), $PhP(OPr^i)_2$ (1·13 mmol), PhONa (1·4 mmol).

* (14) (4%) and (15) (4%). † Products equivalent to (14) and (15), 56 and 28%.

Neither sodium ethoxide nor potassium t-butoxide were active as cocatalysts. The use of a catalytic quantity of sodium carbonate, however, did give reaction but with less specificity of products than when phenoxide was employed. After 16 h at 100° a 57% conversion of benzyl methyl ketone was realised to give (1a) (23%), (2a) (26%), (3a) (3%), and (4a) (48%). A small amount of cyclo-octa-1,5-diene was also formed together with octa-1,3,7-triene and 4-vinylcyclohexene.

Although the same catalyst system has been used previously containing sodium borohydride [7] it has been found not to be essential in the reactions between active methylene compounds and 1,3-dienes. Its presence in some cases, however, does enhance the reactivity of the catalyst.[9] In the absence of sodium phenoxide, benzyl methyl ketone undergoes telomerisation with butadiene when sodium borohydride is used in its place, a 78% conversion is obtained at 75° after 16 h into (1a) (14%), (2a) (13%), (3a) (4%), and (4a) (69%). The role of activation of these cocatalysts is intriguing since it has also been demonstrated that in the presence of nickel acetylacetonate (but not other nickel salts) and di-isopropoxyphenylphosphine, sodium phenoxide can be substituted by phenol and a 85% conversion can be obtained into (1a) (17%), (2a) (20%), (3a) (4%), and (4a) (59%).

Reactions with Other Dienes.—Alkylation of benzyl methyl ketone was also carried out with 1,3-dienes other than butadiene. Treatment of the ketone with a three molar excess of isoprene in the presence of nickel acetylacetonate, di-isopropoxyphenylphosphine and sodium phenoxide in ethanol gave a 32% conversion into (5) (23%), (6) (59%), (7) (3%), and (8) (15%) in 21 h at 100°.

The presence of diastereoisomers was clearly shown in the n.m.r. of (5) (Table 1). In (7), whilst the methyl group at C-9 was readily apparent, assignment to the other methyl group at C-5 was more complex. A signal at τ 8·50 confirms substitution of a methyl group at either C-5 or C-6 but since the non-equivalent methylene protons at C-4 (adjacent to a chiral centre) appear as a doublet of doublets rather than a multiplet, methyl substitution must be at C-5. A similar situation is found in the n.m.r. of (8) but since both methyl groups are clearly attached to olefinic groups the structure is assigned as shown. A number of isoprene dimers were obtained as by-products but their structures were not investigated further.

Similar treatment of 2,3-dimethylbutadiene with benzyl methyl ketone led to an 18% conversion into predominantly one butenyl adduct (10) (94%) and (9) (6%); 2,3,6,7-tetramethylocta-1,3,7-triene (11) was the only hydrocarbon product and constituted 48% by weight of the total products. Only 11% conversion was found in the reaction of penta-1,3-diene and benzyl methyl ketone to give a 4 : 1 mixture of (12) and (13). The two diastereoisomers of (12) were separated by preparative g.l.c. and their n.m.r. spectra obtained (Table 1). Molecular models show that in one of the isomers, the methyl group α to the benzylic position is situated in the environment of the benzene ring and is deshielded. The possibility that these are geometrical isomers rather than diastereioisomers was discounted on the grounds that identical olefinic hydrogen splitting is observed in each case.

Telomerisation with Other Active Methylene Compounds.—A number of other reactions between butadiene and active methylene compounds were successful (Table 3). No

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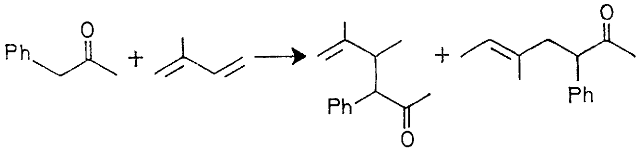
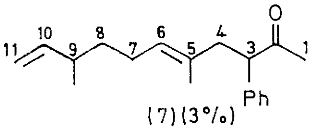
[9] R. Baker, A. H. Cook, and T. N. Smith, *Tetrahedron Letters*, 1973, 503.

reaction occurred between butadiene and phenyl acetaldehyde or ethyl phenylacetate. Whereas compounds such as benzyl methyl ketone and benzyl cyanide reacted with butadiene in the presence of catalytic amounts of the nickel complex, diethyl malonate and ethyl acetoacetate required higher concentrations of catalyst.



(5) (23%) (6) (59%)



(7) (3%)

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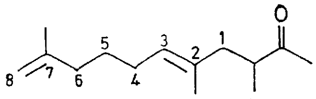
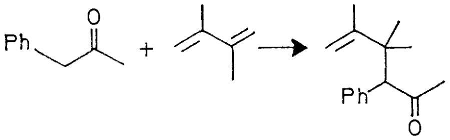


(8) (15%)



(9) (6%)

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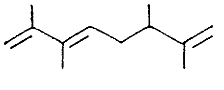

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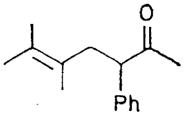
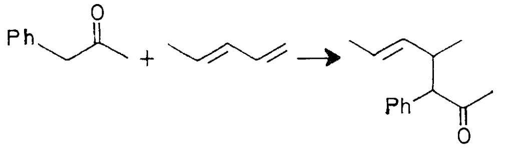
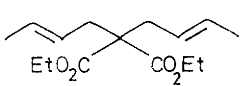


(10) (94%)

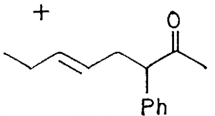


(12) (80%)

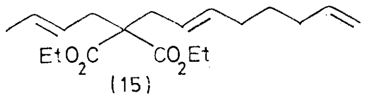
+



(14)



(13) (20%)

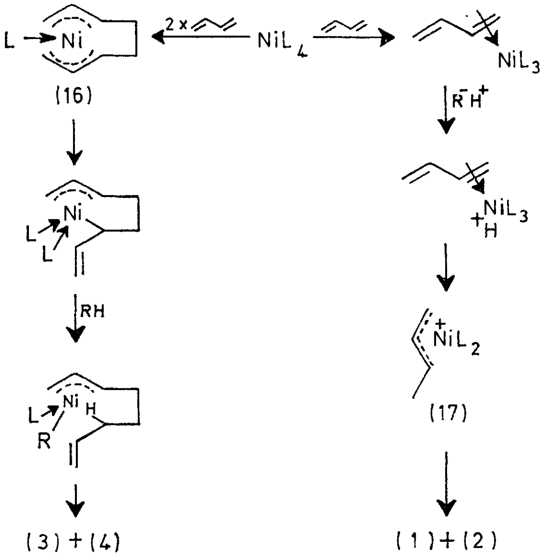


(15)

With diethyl malonate, two other products, (14) (4%) and (15) (4%) were also formed (the diethyl malonate–nickel salt–phosphine ratio was 1 : 0·06 : 0·06). Reaction between butadiene and diethyl malonate can also be achieved by an increase in the amount of phosphine or of sodium phenoxide employed. Thus, no reaction was observed when the ratio substrate–nickel salt–phosphine was 70 : 1 : 1·5 but 96% reaction was found when the ratio phosphine–nickel was 3 : 1. Sodium phenoxide was found to exhibit an analogous activating effect when four times the amount used in the standard conditions was employed. Ethyl acetoacetate exhibited a similar activity to diethyl malonate but acetylacetone gave no observable reaction. 1,3-Dienes other than butadiene, although reactive towards benzyl methyl ketone, appeared to be fairly inert to reaction with β-ketoesters. Nitro-compounds, which have been previously reported to react with palladium catalysts,[10] gave poor or no reaction under the present conditions. With nitroethane and butadiene under the standard conditions at 100°, a trace product was obtained which appeared to be an octadienyl derivative by mass spectroscopy.

DISCUSSION

The reactions are suggested to involve tetrakis(organophosphorus)nickel(0) complexes[11] (Scheme) as previously proposed for reaction of phenol and butadiene.[12] Dialkoxyphenylphosphines have been previously employed by Gray and his co-workers to prepare NiL_4 complexes from nickel halides in refluxing alcohol [L = $PhP(OR)_2$, R = Me or Et].[13] In our *in situ* conditions, the L of NiL_4 probably consists of both 1,3-dienes and phosphine molecules as ligands.



SCHEME

Reaction occurs between butadiene and benzyl methyl ketone in the presence of preformed tetrakis(diisopropoxyphenylphosphine)nickel although a 6 : 1 molar ratio of sodium phenoxide to nickel complex must be employed. This indicates the important role of sodium phenoxide. Previously it has been demonstrated that added base assists the reduction of metal species[14] and

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[10] T. Mitsuyasu, M. Hara, and T. Tsuji, *Chem. Comm.*, 1971, 345.

[11] W. Brenner, P. Heimbach, H. Hey, E. Müller, and G. Wilke, *Annalen*, 1969, **727**, 161.

[12] F. J. Weigert and W. C. Drinkard, *J. Org. Chem.*, 1973, **38**, 335.

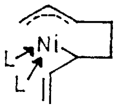
[13] A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chem. Acta*, 1969, **3**, 8.

[14] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

this must be important in our experiments where *in situ* reduction is performed. Evidence for this is found in that $NiBr_2[PhP(OPr)_2]_2$ is only active as a catalyst in the presence of a 6 : 1 excess of sodium phenoxide. However, sodium phenoxide would also assist in the ionisation of the active methylene compound with an increase in reactivity and could enhance formation of a co-ordinately unsaturated species from the tetrakisphosphinenickel species. A weak base such as sodium borohydride can also act as a cocatalyst (Table 3) but the reason for the non-operation of bases such as sodium ethoxide or butoxide is unclear. The successful use of phenol in the presence of nickel acetylacetonate (but not other salts) has been demonstrated, by u.v. spectroscopy, to be due to the production of phenoxide ion in solution.

It is of interest that both dimethoxy- and diethoxyphenylphosphine do not produce an active catalyst for the reaction of benzyl methyl ketone and butadiene. This could be associated with the decreased ease with which these complexes lose a ligand to produce a co-ordinately unsaturated metal complex. Reaction with amines and butadiene is found with these two phosphines, however, although the catalyst system is less reactive than that containing di-isopropoxyphenylphosphine.[15] The presence of amine might enhance formation of a co-ordinately unsaturated species. In general it would appear that the reactivity of amines is higher than that of active methylene compounds and that the activity of the catalyst system decreases with the phosphine, $PhP(OPr)_2 > PhP(OEt)_2 > PhP(OMe)_2$.

In the Scheme (16) has been written as a bis-π-allylnickel derivative [11] but in the presence of tricyclohexylphosphine the structure has been shown to be a σ–π-allyl form, (18) and (19), by n.m.r. evidence.[16,17] A similar situation probably obtains in the case of di-isopropoxyphenylphosphine. The allyl group in (18) could obviously exist in a *syn*- or *anti*-form but the apparently complete formation of the *trans*-isomer (4) would imply the intervention of the *syn*-isomer.[16]



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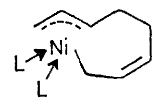

(19)

The hydrocarbons octa-1,3,7-triene and 4-vinylcyclohexene formed as by-products in the telomerisation reaction also arise from (18) and (19).[18] Some vinylcyclohexene could also be formed by a purely thermal reaction.

Formation of the butenyl adducts (1) and (2) arise from the π-allylnickel intermediate (17), which could be obtained by protonation of the complex of butadiene and NiL_3, followed by attack of R^-. Alternatively, oxidative addition of RH would be followed by formation of the π-allylnickel complex and subsequent transfer of the R group. Again the stereochemistry of the allyl derivative must be considered to be a *syn*-π-crotyl intermediate since *trans*-product is obtained. A detailed study has previously been made of the stereochemistry of the π-allylnickel intermediates in the reaction of butadiene and ethylene to form hexa-1,4-diene.[19-21]

It is evident that butenyl adducts are formed to a greater extent in the nickel catalysed reactions of 1,3-dienes with active methylene compounds compared with the previously reported palladium catalysed processes.[6,22] This observation is probably related to the higher basicity [23] of nickel compared to palladium and the relative affinity of the metals for protonation.

The alkylation of benzyl methyl ketone was found to depend on diene concentration, reaction time, and temperature, and the concentration of phosphine and sodium phenoxide. Optimum conversion was obtained when the diene–ketone ratio was 3 : 1. Reducing the amount of diene to a 1 : 1 ratio gave almost exclusive formation of butenyl adduct but the reduction in conversion suggests that the pathway to formation of butenyl adducts is a slower reaction than octadienyl adduct formation. The large fall in conversion at high diene–ketone ratios is presumably an indication of the affinity of butadiene for co-ordination sites on the metal, thus preventing attack by the active methylene compound.

In the standard procedure it was demonstrated in the reaction of benzyl methyl ketone with butadiene, that maximum conversion is reached after 16 h. Prolonged heating produces only hydrocarbons but the isomer distribution of C_4 and C_8 remained fairly constant. This result together with control experiments carried out with isolated butenyl and octadienyl adducts, proved that no isomerisation takes place. This contrasts with the adducts of phenols [12] and amines [15] which did isomerise to a considerable extent in the presence of catalyst. Formation of a carbon–carbon bond is, therefore, irreversible under the present conditions whereas both the carbon–oxygen and carbon–nitrogen bond are formed reversibly.

Maximum conversions were also obtained when di-isopropoxyphenylphosphine was employed in a phosphine–nickel ratio of 3 : 1 which is strong evidence that a species such as NiL_3 is important in the process. At the 3 : 1 ratio of phosphine–nickel, however, more

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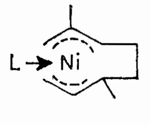
butenyl adducts were obtained than at lower ratios so that the standard procedure employed a phosphine–nickel ratio of 1·5 : 1. With change in phosphine concentration, a clear trend is seen in the variation of product distribution. Increased concentration of phosphine induces greater competition between ligand and butadiene for co-ordination sites on the metal and formation of butenyl adducts is favoured.

The activity of the catalyst system is affected by the nickel salt and the order of reactivity was: $NiBr_2 \sim NiCl_2 > Ni(acac)_2 > Ni(hexanoate)_2 > Ni(acetate)_2 > Ni(laurate)_2$. Two factors could govern the reactivity of the nickel salts. The ease of reduction of Ni^{II} to Ni^0 could be affected by the associated anions. This is certainly the case since, although measurements have been made in a different solvent (dimethoxyethane), electrochemical data confirms the greater ease of reduction of nickel chloride compared to nickel acetylacetonate.[24] Whilst this is true, it is also possible that the reactivity of the intermediates may be affected by the different anions present in solution. Evidence for this is provided in that the rates of reactions of π-allylpalladium derivatives with dienes are affected by bridging anions [25] and the rates of palladium catalysed reactions of unsaturated compounds are influenced by ligands bound to the metal.[26] Nickel bromide produced a highly reactive catalyst system with di-isopropoxyphenylphosphine which was demonstrated by a 'flow system' experiment. A catalyst comprising nickel salt, di-isopropoxyphenylphosphine, and sodium phenoxide was placed in ethanol and butadiene passed through the agitated solution maintained at 100°. A butadiene flow rate of 60 ml min^{-1} produced 57% reaction after 2·25 h and 64% reaction after 9 h. Equal amounts of branched and linear butenyl adducts were almost exclusively formed presumably due to the small contact time between diene and catalyst resulting in a low diene–ketone ratio. No corresponding reaction occurred using nickel acetylacetonate.

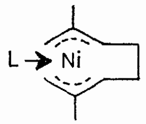
Reactions of Substituted 1,3-*Dienes*.—Large differences in the reactivity of substituted 1,3-dienes were found with benzyl methyl ketone.

Isoprene is the only diene other than butadiene which yields 2 : 1 adducts and the ease of the reaction decreases markedly with increasing alkyl substitution. With isoprene, the two 2 : 1 adducts obtained were derived from head-to-tail and tail-to-tail dimerisation of isoprene. Formation of these products would require the intermediacy of the corresponding bis-π-allylnickel derivatives (20) and (21). A larger amount of 2 : 1 adduct obtained from (21) possibly reflects a greater stability of this intermediate compared to (20). Steric factors must also be important, however, and the lack of 2 : 1 adducts and decrease in reactivity of substituted dienes show that this factor is dominant. No reaction was obtained with substituted dienes such as myrcene and 2,5-dimethylhexa-2,4-diene.

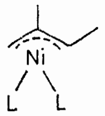
Formation of the 1 : 1 adducts is governed by the π-allylnickel intermediate formed and also by the position of attack on this intermediate by the active methylene compound. An equal distribution of branched and linear butenyl products is obtained from butadiene. Two π-allylmetal derivatives could be produced from isoprene but the products appear to be derived exclusively from (22). 2,3-Dimethylbutadiene can produce only one π-allylmetal derivative (23) and reaction occurs predominantly at the primary position. The symmetrical π-allylnickel species (24) must be the origin of the major product formed from piperylene, but formation of the minor product must involve (25).



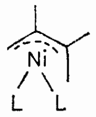
(20)



(21)

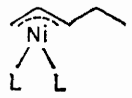


(22)



(23)

(24)



(25)

Reactions of Other Active Methylene Compounds.—A range of active methylene compounds have been shown to react with butadiene in the presence of palladium catalysts and some correlation with pK_a was observed.[6] In the present reactions the range of reactivity was smaller. Thus, although reaction was found between buta-1,3-diene and benzyl methyl ketone or benzyl cyanide, no reaction took place with ethyl phenylacetate or phenyl acetaldehyde. A small amount of an octadienyl adduct was obtained from buta-1,3-diene and nitromethane when the catalyst system containing nickel was used.

Whereas compounds such as benzyl methyl ketone and benzyl cyanide react in the presence of catalytic amounts of Ni^0 complex, diethyl malonate and ethyl acetoacetate failed to react under the same conditions. However, if one of three conditions is met, reaction does proceed between butadiene and these esters: (*a*) an increase in the amount of nickel salt and phosphine; (*b*) a change in the phosphine–nickel ratio from 1·5 : 1 to 3 : 1; (*c*) an increase of sodium phenoxide cocatalyst added relative to nickel (*e.g.* from 2 : 1 to 6 : 1). We propose that complex formation between the β-ketoester or diester and the nickel complex prevents reaction at low catalytic levels. Support for this is found in the observation that introduction of an equimolar quantity of diethyl malonate or ethyl acetoacetate into the telomerisation reaction of benzyl methyl ketone and

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butadiene completely arrested alkylation. Thus the esters appear to complex with the nickel catalyst preventing any further catalytic activity. The observations (*a*)—(*c*) are three ways in which this intermediate complex can be activated. No alkylation of acetylacetone catalysed by nickel complexes occurs under any of the conditions which suggests the greater stability of the nickel–acetylacetone complex formed in the reaction.

It has recently been reported that complexes can be made under mild conditions between metal salts and acetylacetone, ethyl acetoacetate, or diethyl malonate.[27,28] Spectral analysis of these complexes has revealed that the diketone and ketoesters are acting as neutral ligands. It is suggested, therefore, that in the reaction of diethyl malonate or ethyl acetoacetate and butadiene, complexation occurs between substrate and metal involving neutral ligands subsequent to diene and phosphine co-ordination. The use of method (*a*) to induce reaction between diethyl malonate and diene gives high yield of butenyl adducts together with some dibutenyl adducts. A satisfactory catalyst level employed was with the diethyl malonate–nickel acetylacetonate–di-isopropoxyphenylphosphine ratio 1 : 0·06 : 0·06. Use of either of the other methods again yielded butenyl adducts. Methods (*a*) and (*b*) effectively reduce the competition for co-ordination sites between phosphine and neutral reactant, and the catalytic nickel–phosphine complex is more readily formed. Method (*c*) probably originates from the fact that the role of sodium phenoxide assists the reduction of the Ni^{II} salt to the active catalyst species.[14] It could also have an effect in breaking down the complexation between the catalyst complex and the ketone or ester containing reagents. The greater proportion of butenyl products formed in these reactions is considered to originate from the complexing property of these reagents.

Complexation to the catalytic intermediate could also be responsible for the lack of reaction with the nitro-derivatives. Evidence for this was provided by an experiment in which nitroethane addition was shown effectively to prevent reaction between benzyl methyl ketone and butadiene.

EXPERIMENTAL

Reactions were performed under nitrogen in sealed Carius tubes which were placed in constant temperature oil-baths. Solvents, where applicable, were purged with nitrogen before use. Reactant active methylene compounds were used as supplied without further purification. Butadiene was passed over potassium hydroxide pellets to remove the inhibitor and moisture and distilled into the reaction vessel on a vacuum line. Higher boiling dienes were purified by distillation.

A Pye 104 chromatograph was employed for all g.l.c. analysis (nitrogen carrier gas through 5 ft × 0·25 in glass column, 10% E301) and a Pye 105 chromatograph for all preparative g.l.c. (nitrogen carrier gas through 15 ft × 0·375 in glass column, 25% E301). Peak areas were measured by a fixed arm planimeter or by calculation. Yields are expressed in terms of percentage conversion of active methylene compound. N.m.r. spectra were obtained with a Perkin-Elmer R12 instrument using tetramethylsilane as internal standard and carbon tetrachloride as solvent.

Di-isopropoxyphenylphosphine was prepared according to Rabinowitz and Pellon [29] and purified by distillation under reduced pressure, b.p. 83—85° at 0·6 mmHg, $\nu_{max.}$ (Nujol) 3000, 1460, 1445, 1385, 1240, 1180, 1140, 1115, 995, 965, 880, 750, and 700 cm^{-1}. 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.

General Procedure.—A mixture of anhydrous nickel acetylacetonate (0·75 mmol), di-isopropoxyphenylphosphine (1·13 mmol), sodium borohydride (0·3 mmol), benzyl methyl ketone (0·05 mol), and butadiene (0·15 mol) was heated in ethanol (12 ml) for 16 h at 75°. Filtration through Kieselguhr gave a 90% conversion into (1a) (15%), (2a) (19%), (3a) (4%), and (4a) (62%) together with traces of octa-1,3,7-triene and 4-vinylcyclohexene. Distillation gave a mixture of (1a) and (2a), a fraction consisting of mainly (4a) but also some (1a) and (2a), and a final fraction which was the adduct (4a) in >95% purity. Separation of (1a) and (2a) was achieved by preparative g.l.c. at 150° with gas flow 100 ml min^{-1}. N.m.r. spectra are summarised in Table 1; compound (1a) *m/e* 288 (2%, M^+), 145 (96), 134 (43), 117 (32), 105 (22), 91 (50), 55 (25), 43 (100), 41 (20), 39 (21), and 27 (18), $\nu_{max.}$ 3000, 1710, 1640, 1600, 1500, 1460, 1360, 1160, 920, 760, and 700 cm^{-1}; compound (2a) *m/e* 228 (2%, M^+), 145 (85), 134 (18), 117 (38), 105 (25), 97 (65), 91 (63), 77 (18), 55 (19), 43 (100), 41 (21), and 39 (25), $\nu_{max.}$ 3000, 1710, 1640, 1600, 1500, 1460, 1360, 1160, 970, 760, and 700 cm^{-1}; compound (3a) *m/e* 242 (5%, M^+), 134 (100), 129 (20), 119 (32), 117 (41), 91 (80), 67 (42), 55 (28), 43 (84), 42 (44), and 40 (20); compound (4a) *m/e* 242 (19%, M^+), 134 (60), 128 (21), 117 (81), 104 (20), 95 (34), 91 (100), 67 (37), 43 (69), and 42 (27), $\nu_{max.}$ 2900, 1710, 1640, 1600, 1500, 1460, 1440, 1360, 1160, 880, 920, 760, and 700 cm^{-1}.

This general procedure was used for the series of experiments with changes in conditions as summarised in Tables 2 and 3.

Reaction of Butadiene with Other Active Methylene Derivatives.—Benzyl cyanide. Benzyl cyanide gave a 30% reaction with butadiene after 16 h at 100° to yield (1b) (10%), (2b) (11%), (3b) (15%), and (4b) (59%) and the latter was separated by distillation, τ (CCl_4) 2·70 (5H, s, aromatic), 4·05—4·75 (3H, m, vinylic), 4·85—5·30 (2H, m, terminal olefinic), 6·30 (1H, t, *J* 8 Hz, benzylic), 7·50 (2H, m, allylic, α-benzylic), 8·10 (4H, m, allylic), and 8·50 (2H, m, methylene), *m/e* 224 (9%, M^+), 117 (92), 116 (31), 99 (73), 89 (15), 81 (14), 67 (80), 41 (100), 39 (30), and 27 (17), $\nu_{max.}$ 3000, 2260, 1640, 1600, 1505, 1460, 980, 920, 750, and 700 cm^{-1}. Other derivatives were characterised by the comparison of g.l.c. retention times with the similar adducts of benzyl methyl ketone.

Diethyl malonate. With a diethyl malonate–nickel salt–phosphine ratio of 1 : 0·06 : 0·06, 96% reaction with butadiene was found at 100° after 16 h to give a mixture of (1c) (39%), (2c) (35%), (3c) (3%), (4c) (13%), (14) (4%), and (15)

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(4%). After extraction, distillation gave three fractions which contained butenyl adducts, a mixture of mainly dibutenyl and octadienyl adducts, and octadienyl adducts and higher telomer, respectively. Final separation was by preparative chromatography to give (1c)—(4c) and (14), whose spectroscopic properties have been previously reported,[4,6] and (15), τ (CCl_4) 4·00—4·80 (5H, m, vinylic, 4·80—5·30 (2H, m, terminal olefinic), 5·90 (4H, q, J 7 Hz, methylene), 7·55 (4H, d, J 6 Hz, allylic), 8·00 (4H, m, allylic), 8·40 (2H, m, methylene), 8·35 (3H, d, J 5 Hz, methyl), and 8·75 (6H, t, J 7 Hz, methyl), m/e 322 (3%, M^+), 267, (25), 175 (30), 167 (35), 79 (26), 67 (38), 55 (55), 41 (45), 29 (100), and 27 (23), $\nu_{max.}$ 3000, 1730, 1645, 1460, 1205, 970, 920, and 870 cm^{-1}.

Ethyl acetoacetate. Ethyl acetoacetate (0·05 mol) reacted with butadiene (0·15 mol) in the presence of nickel acetylacetonate (0·025 mol), sodium phenoxide (0·03 mol), diisopropoxyphenylphosphine (0·025 mol), and ethanol (10 ml) for 15 h at 100° to give a quantitative yield of (4d) (16%) and two products equivalent to (14) and (15) comprising 56 and 28% of the product mixture. Separation was by distillation and preparative chromatography and physical characteristics have been previously reported.[4,6]

Reaction of Benzyl Methyl Ketone with Other Dienes.—*Isoprene*. Treatment of benzyl methyl ketone (0·05 mol) with isoprene (0·15 mol) in the presence of butanol (12·0 ml), according to the standard procedure at 100° for 2 h, afforded a 32% conversion into (5) (23%), (6) (59%), (7) (3%), and (8) (15%). The reaction mixture consisted of four hydrocarbons in relative amounts 1 : 1 : 5 : 1 (18%) and the major isomer was assigned by n.m.r. as 2,7-dimethylocta-1,3,7-triene. Distillation of the crude reaction mixture, after filtration, gave fractions containing butanol and four hydrocarbon products (9·2 g), mainly hydrocarbons, hydrocarbons and recovered benzyl methyl ketone, (5) and (6), a mixture of 1 : 1 and 2 : 1 isoprene–benzyl methyl ketone in the ratio 4 : 1, and (7) and (8). Final purification of the fractions was achieved by preparative g.l.c.: compound (5) m/e 202 (5%, M^+), 159 (87), 158 (33), 134 (85), 117 (64), 105 (15), 91 (38), 69 (30), 43 (100), 41 (37), and 39 (12); compound (6) 202 (26%, M^+), 159 (53), 134 (63), 131 (32), 117 (100), 111 (41), 91 (65), 77 (27), 43 (88), and 41 (62); compound (7) 270 (29%, M^+), 134 (95), 131 (40), 123 (22), 105 (22), 95 (31), 91 (66), 81 (69), 55 (42), 43 (100), and 41 (35); compound (8) m/e 270 (35%, M^+), 175 (51), 134 (100), 131 (46), 95 (35), 91 (73), 81 (62), 55 (24), 43 (54), and 41 (32).

2,3-*Dimethylbutadiene*. Reaction of benzyl methyl ketone (0·05 mol) with 2,3-dimethylbutadiene (0·15 mol) in butanol (12·0 ml) for 38 h at 100° according to the standard procedure gave 18% conversion into (9) (6%) and (10) (94%). Distillation, after filtration, produced fractions containing recovered benzyl methyl ketone, a mixture of benzyl methyl ketone, hydrocarbon, and (10), and a mixture containing (9), (10), and (11) identified as 2,3,6,7-tetramethylocta-1,3,7-triene from the mixed n.m.r. spectrum. A pure sample of (10) was obtained by preparative g.l.c., m/e 216 (18%, M^+), 134 (100), 131 (19), 91 (20), 83 (47), 55 (32), 43 (19), and 41 (27), $\nu_{max.}$ 3000, 1710, 1670, 1600, 1460, 1380, 1160, 760, and 700 cm^{-1}.

trans-*Piperylene*. Reaction of benzyl methyl ketone (0·05 mol) with *trans*-piperylene (0·15 mol) in butanol (12·0 ml) according to the standard procedure at 100° for 40 h, gave an 11% conversion into (12) (80%) and (13) (20%). A mixture of four hydrocarbons was produced which was not studied further. Initial distillation of the reaction solution at atmospheric pressure effected separation of solvent and unchanged piperylene. Fractional distillation afforded good separation of each diene–benzyl methyl ketone adduct. The first fraction contained only hydrocarbons, but further heating gave a fraction containing mostly benzyl methyl ketone and a trace of adducts followed by a clear liquid containing an equal amount of benzyl methyl ketone and C_5 adducts. Further fractions comprised, in the main, the two forms of (12) and (13), and finally one containing a higher proportion of one of the isomers (12) and (13). Preparative g.l.c. at 230° effected good separation of the isomers (12): isomer (12A) m/e 202 (11%, M^+), 159 (15), 134 (100), 117 (30), 115 (12), 91 (31), 69 (72), 43 (45), 41 (45), and 39 (16); isomer (12B) m/e 202 (13%, M^+), 159 (17), 135 (15), 134 (100), 117 (38), 115 (17), 91 (43), 69 (88), 43 (55), and 39 (20); compound (13) m/e 202 (16%, M^+), 159 (23), 134 (48), 117 (100), 115 (20), 111 (53), 105 (28), 91 (87), 55 (21), 43 (67), and 41 (32).

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