

## Formation of Alcohols from the Reactions of Buta-1,3-diene and Isoprene with Aldehydes catalysed by Nickel Complexes

By Raymond Baker\* and Michael J. Crimmin, Chemistry Department, The University, Southampton SO9 5NH

The reaction of buta-1,3-diene with acetaldehyde, benzaldehyde, and acrolein in the presence of bis(1,5-cyclo-octadiene)nickel and an organophosphorus ligand has been demonstrated to yield 2 : 1 adducts. With triphenylphosphine as ligand high selectivity to 1-substituted-3,6,8-nonatrien-1-ols was found. A similar reaction between isoprene and acetaldehyde in the presence of (cyclododecatriene)nickel and triphenylphosphine gave mainly 2 : 1 adducts in which the isoprene was dimerised in a head-tail manner. The major products were 3,7-dimethyl-3-vinylocta-7-en-2-ol and its isomer 3,7-dimethyl-3-vinylocta-6-en-2-ol. The selectivity of this reaction is discussed in terms of the  $\sigma,\eta$  character of the bis( $\eta$ -allyl)nickel intermediate.

SINCE the initial work by Corey and Semmelhack<sup>1,2</sup> a number of reports have appeared of the reactions of  $\eta$ -allylnickel halides with aldehydes and ketones.<sup>3,4</sup> Intramolecular<sup>5</sup> and intermolecular<sup>6</sup> reactions of  $\alpha$ -(2-ethoxycarbonylallyl)nickel bromide with aldehydes and ketones have been employed in the synthesis of  $\alpha$ -methylene- $\gamma$ -lactones. Reactions with bis( $\eta$ -allyl)nickel<sup>7</sup> and  $\alpha\omega$ -dodecatriendiylnickel<sup>8</sup> have been shown to yield alcohols on reaction with aldehydes.

In contrast to the reactions of conjugated dienes with nucleophilic reagents in the presence of metal complex catalysts, reactions with carbonyl compounds have received much less attention.<sup>9,10</sup> Products from 1 mol of butadiene and 2 mol of an aldehyde or ketone were formed on bubbling butadiene through a suspension of bis(cyclo-octadiene)nickel in the carbonyl species.<sup>7,11</sup> Catalytic reactions of 1,3-dienes with ketones in the presence of a nickel-ligand system with formation of tertiary alcohols have been reported by Akutagawa.<sup>12</sup> Palladium-complex-catalysed reactions of buta-1,3-diene with aldehydes and formation of secondary alcohols have also been studied.<sup>13-16</sup>

We now wish to report the formation of alcohols from reactions of butadiene with acetaldehyde, benzaldehyde, and acrolein catalysed by bis(cyclo-octadiene)nickel in which a series of 2 : 1 adducts are formed with good selectivity. The reaction of isoprene with acetaldehyde in the presence of (cyclododecatriene)nickel has also been studied and the 2 : 1 adducts formed have been shown to be derived from specific head-tail dimerisation of isoprene.

### RESULTS AND DISCUSSION

Acetaldehyde (50 mmol) and butadiene (250 mmol) were reacted in the presence of bis(cyclo-octadiene)nickel (12.5 mmol) and an organophosphorus ligand at 0 °C

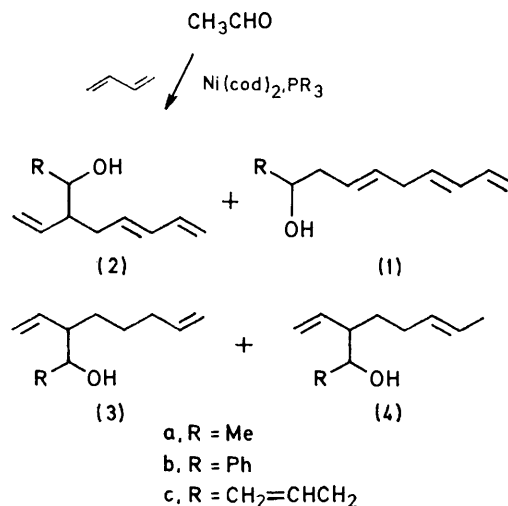
TABLE I

Reaction<sup>a</sup> of butadiene and acetaldehyde in the presence of bis(cyclo-octadiene)nickel<sup>b</sup>

Organophosphorus ligand	% Reaction <sup>c</sup>	Product (%)			
		(1)	(2)	(3)	(4)
PPh <sub>3</sub>	105	71	12	5	4
PBu <sub>3</sub>	26	40	19	26	8
P(cyclohexyl) <sub>3</sub>	33	3	29	40	18
P(OPh) <sub>3</sub>	< 3				

<sup>a</sup> 0 °C, 16 h. <sup>b</sup> Ni(cod)<sub>2</sub> (12.5 mmol), organophosphorus ligand (12.5 mmol), acetaldehyde (50 mmol), and butadiene (250 mmol). <sup>c</sup> Based on Ni(cod)<sub>2</sub>.

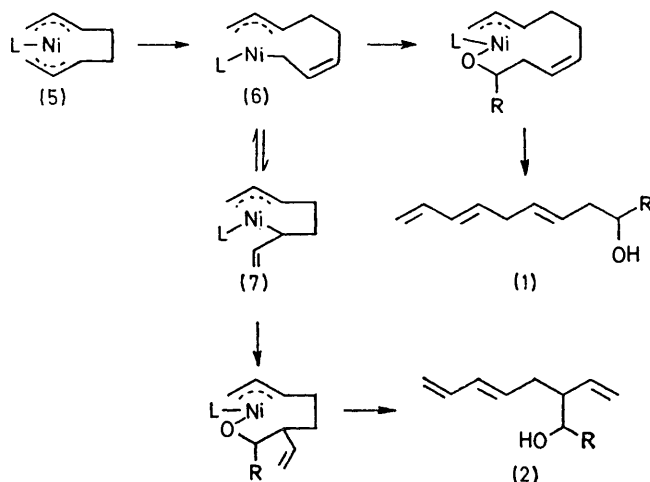
for 16 h. A mixture of products (1)–(4) was formed whose ratio was dependent upon the ligand employed (Table I). Isolation of products was carried out by column chromatography or distillation followed by preparative g.l.c. and structures identified on the basis of spectral properties.



The greatest overall reaction occurred with a 1 : 1 ratio of triphenylphosphine : nickel complex and the relative amounts of linear and branched-chain alcohols could be changed from >70% linear to 85% branched product with triphenylphosphine and tricyclohexylphosphine, respectively. The use of triphenylphosphine also led to the most selective reaction, with formation of (1) in over 70% yield, whereas with tri-*n*-butylphosphine an approximately 1 : 1 mixture of linear to branched-chain alcohols was observed. However yields were also obtained in the presence of the other organophosphorus ligands.

These observations are consistent with reaction occurring through the intermediates (5)–(7) (Scheme 1). Although trienols were the predominant products in the presence of triphenylphosphine, substantial amounts of dienols were formed in the presence of tri-*n*-butyl- and tricyclohexylphosphine. The former are formed by Ni-H elimination which can occur under the reaction conditions, whereas the latter can only be formed by protonation on the addition of aqueous potassium cyanide in the work-up procedure. In the presence of

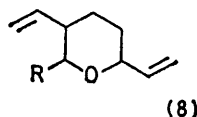
basic ligands such as tri-*n*-butyl- or tricyclohexylphosphine the bis( $\eta$ -allyl)nickel intermediate (5) has been suggested to exist predominantly in the  $\sigma,\eta$  forms



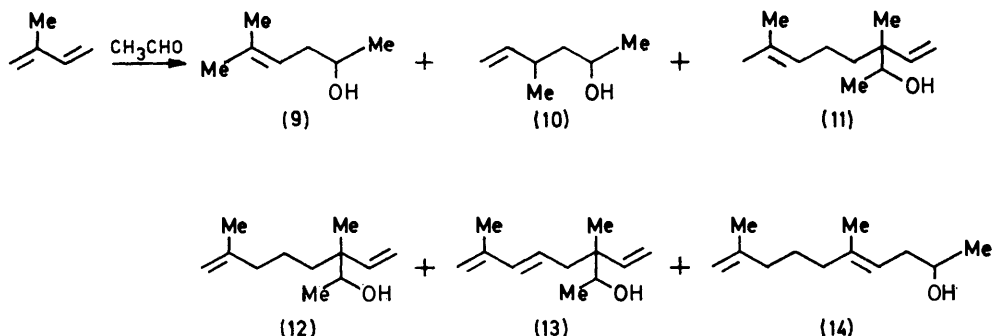
SCHEME 1

(6) and (7).<sup>17-20</sup> A combination of steric and electronic effects could then be involved in determining the product ratios. Although tri-*n*-butyl- and tricyclohexylphosphine have similar donating abilities,<sup>21</sup> the larger steric bulk of the latter would direct the reaction through (7) rather than (6), and thus lead to larger amounts of (2).

Similar reactions of butadiene with acrolein and benzaldehyde have also been studied in the presence of bis(cyclo-octadiene)nickel and triphenylphosphine. In the case of acrolein a 79% conversion (based on nickel complex) to products was obtained which consisted of over 80% of (1c). Reaction with benzaldehyde gave a 77% yield of (1b). This is to be contrasted with a similar reaction<sup>22</sup> in which the catalyst was formed by reduction



of nickel chloride with sodium borohydride in the presence of triphenylphosphine and butadiene. In this



case the major product was found to be the pyran (8). This result indicates the importance of ligand and other effects in product control. The reactions of butadiene

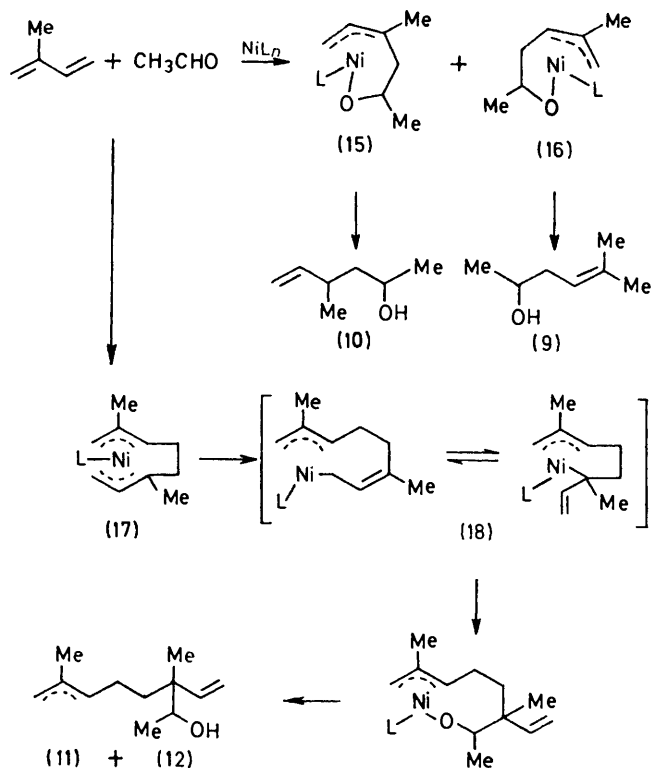
and aldehydes catalysed by palladium complexes have been shown to yield either a mixture of the isomeric pyrans (8) or (2) depending upon the ratio of triphenylphosphine and palladium salt in the catalyst.<sup>14-16</sup> This sharp change in product formation with relative catalyst concentration was not observed in the present reactions and lower yields of product were obtained when a 4 : 1 ratio of triphenylphosphine to bis(cyclo-octadiene)nickel was employed.

**Reactions of Isoprene with Acetaldehyde.**—No reaction of isoprene with acetaldehyde was found in the presence of bis(cyclo-octadiene)nickel and triphenylphosphine at 0 °C. Reaction occurred, however, in the presence of (cyclododecatriene)nickel. Isoprene was added to a solution of cyclododecatrienickel and triphenylphosphine at -20 °C and after stirring overnight followed by the addition of acetaldehyde (90 mmol), the solution was allowed to reach room temperature and the reaction quenched by the addition of aqueous potassium cyanide. Extraction gave the mixture of products, (9) (12%), (10) (22%), (11) and (12) (56%), (13) (3%), and (14) (7%). Separation of the 1 : 1 adducts (9) and (10) from the 2 : 1 adducts (11)—(14) was readily achieved by column chromatography in 19 and 37% yields, respectively. The 2 : 1 adducts, which consisted of >85% of (11) and (12) were further separated by preparative gas chromatography. In the presence of tricyclohexylphosphine as ligand, only small amounts of 1 : 1 adducts were obtained and the 2 : 1 adducts consisted of  $\geq 95\%$  (11) and (12). The 2 : 1 adducts were identified by their spectral data, particularly their n.m.r. spectra. For (11), four methyl groups are indicated, two virtually equivalent at  $\tau$  8.30 and 8.40, one as a doublet at  $\tau$  8.95 assigned  $\beta$  to the OH, and finally a singlet at  $\tau$  9.05 which must be situated on a saturated carbon atom. The olefinic signals are also consistent with the structure assigned and evidence for the vinyl group is also found in the i.r. spectrum at 3 080, 1 635, and 910  $\text{cm}^{-1}$ .

The n.m.r. spectrum for (12) shows similarities but an isopropylidene group is indicated in place of two olefinic methyl groups. This is shown by a broad singlet at  $\tau$  5.40 for two protons due to the terminal olefinic protons and a single methyl group at  $\tau$  8.30. This

grouping is again confirmed by the i.r. spectrum in which two peaks now appear at 885 and 915  $\text{cm}^{-1}$  for the terminal vinylic C-H bands.

The 1 : 1 adducts (9) and (10) probably arise through the intermediates (15) and (16) (Scheme 2). The 2 : 1 adducts would appear to be derived from the bis- $\eta$ -allyl-nickel complex (17). Furthermore, X-ray and n.m.r.



SCHEME 2

studies have already shown that, in the presence of certain ligands, the structure of (17) is more closely represented as a ( $\sigma,\eta$ -allyl)nickel species (18).<sup>23</sup> The structures of the 2 : 1 adducts indicate that reaction is occurring with high specificity at the  $\sigma$ -allyl site.

Previous studies have also indicated that, in reactions of amines and active methylene compounds with isoprene, products also arise through the intermediate (17) and, in these cases, reaction occurs preferentially at the  $\eta$ -allyl moiety.<sup>24, 25</sup> These observations that a bis( $\eta$ -allyl)metal intermediate, which has the ability to exist as a  $\sigma,\eta$ -allyl structure, displays regioselectivity of reaction towards nucleophilic and electrophilic reagents, has also been found in the nickel-complex-catalysed reactions of allene.<sup>26</sup> In this case the intermediate (19), obtainable from oligomerisation of three molecules of allene, has also been shown to be best represented as the  $\sigma,\eta$ -form (20). Again reactions of electrophilic and



nucleophilic reagents occurred preferentially at the  $\sigma$ - and  $\eta$ -allyl sites, respectively.

## EXPERIMENTAL

Anhydrous nickel acetylacetonate was obtained by dehydration of the dihydrate by heating *in vacuo* at 80 °C and 1 mmHg for 16 h. Cyclo-octa-1,5-diene was distilled and stored over molecular sieves before use. Triphenylphosphine was recrystallised from benzene–light petroleum and tricyclohexylphosphine was prepared as described by Issleib and Brack<sup>27</sup> and isolated as the carbon disulphide adduct. This was stored without deterioration, and, when required, the phosphine (m.p. 74–78 °C) was liberated by heating at 100 °C and 20 mmHg. All other reagents were used as supplied.

A solution of bis(cyclo-octadiene)nickel was prepared as described.<sup>28</sup>

TABLE 2

Hydrogen-1 n.m.r. data for products of the reaction of butadiene with aldehydes ( $\tau$ )

Proton	Product		
	(1a)	(1b)	(1c)
Aromatic			2.70 (5 H, m)
Vinyl	3.20–4.70 (5 H, m)	3.10–4.65 (6 H, m)	3.50–4.80 (5 H, m)
Terminal olefinic	4.70–5.20 (2 H, m)	4.65–5.10 (4 H, m)	4.80–5.20 (2 H, m)
$\alpha$ -OH	6.30 (1 H, m)	5.85 (1 H, m)	5.40 (1 H, m)
Allylic	7.15 (2 H, m)	7.10 (2 H, m)	7.20 (2 H, m)
Allylic	7.85 (2 H, m)	7.66 (2 H, m)	7.55 (2 H, m)
OH	7.45 (1 H, br s)	7.90 (1 H, br s)	8.00 (1 H, br s)
Methyl	8.95 (3 H, d, J 7 Hz)		

*Reaction of Butadiene with Aldehydes.—Acetaldehyde.* Triphenylphosphine (2.29 g, 9.1 mmol) in benzene solution was added to bis(cyclo-octadiene)nickel, Ni(cod)<sub>2</sub> (2.51 g, 9.1 mmol). The solution was stirred for 30 min at 0 °C before the addition of butadiene (20 ml). The solution rapidly turned a clear dark red, and after 30 min acetaldehyde (1.4 g, 32 mmol) was added. After stirring for 16 h at 0 °C aqueous potassium cyanide was added and the products extracted with ether. Fractional distillation gave a crude separation into hydrocarbon (0.70 g), b.p. 40–50 °C at 12 mmHg, a mixture of predominantly (1a) and (2a) (1.11 g, b.p. 110–120 °C at 12 mmHg), and (1a) (0.35 g, b.p. 120–122 °C at 12 mmHg) (Found: C, 67.61%; H, 8.71%. C<sub>15</sub>H<sub>21</sub>O<sub>4</sub> requires C, 67.39%; H, 8.67%; analysed as the diethyl malonate ester). Combined quantities of (1a) and (2a) represented a 105% conversion based on Ni(cod)<sub>2</sub>. Further separation of (1a) and (2a) was achieved by chromatography on silica gel using light petroleum–ether as eluant. The branched alcohol (2a)<sup>16</sup> was eluted before (1a) in the solvent range 15–25% ether in light petroleum. N.m.r. details are recorded in Table 2 and further spectral characteristics for (1a) are; *m/e* 152 (6%, M<sup>+</sup>), 105 (41), 93 (50), 91 (50), 79 (84), 77 (31), 67 (35), 45 (100), and 41 (39);  $\nu_{\max}$ . 3 350, 3 080, 1 645, 1 605, 1 440, 1 375, 1 080, 1 005, 970, and 945 cm<sup>-1</sup>.

Small quantities of (3) and (4) were obtained by preparative gas chromatography of the distilled 2 : 1 adduct fractions on 15% Carbowax 20M (15 ft  $\times$  0.375 in, 60–80 mesh Diatomite): (3),  $\tau$ (CCl<sub>4</sub>), 4.00–4.60 (2 H, m, vinylic), 4.70–5.15 (4 H, m, terminal olefinic), 6.40 (1 H, m,  $\alpha$ -OH),

7.80—8.20 (3 H, m, allylic methylene + allylic methine), 8.40—8.70 (5 H, m, methylenes and OH), and 8.85 (3 H, d,  $J$  7 Hz, Me); (4),  $\tau(\text{CCl}_4)$ , 4.00—5.20 (5 H, m, olefinic), 6.40 (1 H, m,  $\alpha$ -OH), 7.80—8.20 (3 H, m, allylic methylene + allylic methine), 8.30—8.50 (3 H, m, Me), 8.50—8.80 (3 H, m, methylene + OH), and 8.90 (3 H, d,  $J$  7 Hz, Me). Further gas chromatographic studies indicated that (2a), (3), and (4) each consisted of two diastereoisomers although these were not separated preparatively.

**Benzaldehyde.** The butadiene-nickel complex was prepared as above from bis(cyclo-octadiene)nickel (3.8 mmol) and benzaldehyde (3.2 g, 30 mmol) was added. After the addition of aqueous potassium cyanide solution and ether extraction a crude product mixture (3.77 g) was obtained. The mixture was chromatographed on silica using ether-light petroleum. The alcohol (1b) (1.63 g, 77%) was eluted with ether-light petroleum (25 : 75) and was distilled, b.p. 210—220 °C at 12 mmHg (Found: C, 83.97%; H, 8.47%.  $\text{C}_{15}\text{H}_{18}\text{O}$  requires C, 84.07% H, 8.47%);  $m/e$  214 (1%,  $M^+$ ) 108 (19), 107 (100), 105 (17), 91 (14), 79 (91), 77 (32), 41 (12), and 39 (12);  $\nu_{\text{max}}$  3 600—3 140s, 3 030s, 2 905s, 1 680m, 1 650m, 1 600m, 1 495s, 1 130—950s, 905m, 760s, and 705s  $\text{cm}^{-1}$ .

**Acrolein.** The butadiene-nickel complex was prepared as above from bis(cyclo-octadiene)nickel (8.9 mmol) and acrolein (1.68 g, 30 mmol). The crude product mixture (5.64 g) was chromatographed on silica gel using ether-light petroleum mixtures. The alcohol (1c) (1.16 g, 79%) was eluted with ether-light petroleum (25 : 75) (Found C, 79.66%; H, 9.91%.  $\text{C}_{11}\text{H}_{16}\text{O}$  requires C, 80.44%, H, 9.82%);  $m/e$  164 (8%,  $M^+$ ), 117 (28), 108 (54), 105 (39), 93 (36), 92 (55), 80 (100), 79 (87), and 57 (45);  $\nu_{\text{max}}$  3 620—3 160s, 3 080m, 3 010s, 3 000—2 840s, 1 645s, 1 600w, 1 430s, 1 120m, 1 080—960s, 915s, 785w, and 730m  $\text{cm}^{-1}$ .

**Reaction of Isoprene with Acetaldehyde.**—Diethylaluminum ethoxide [prepared from triethylaluminum (4.30 g, 25.6 mmol) and ethanol (1.18 g, 25.6 mmol)] was added slowly to a mixture of anhydrous nickel acetylacetonate (5.0 g, 19.3 mmol) and *trans,trans,trans*-cyclododecatriene (6.75 g, 42 mmol) in sodium-dried ether (25 ml) at 0 °C. The solution was stirred for a further 17 h at 0 °C and triphenylphosphine (14.5 mmol) was then added. The solution was cooled to -20 °C and after the addition of isoprene (20 ml) the mixture was stirred for 16 h. Acetaldehyde (5 ml, 90 mmol) was added and the solution allowed to reach room temperature during 8 h. The reaction was terminated by the addition of aqueous potassium cyanide solution and the products extracted with ether; g.l.c. analysis indicated the composition (9) (12%), (10) (22%), (11) and (12) (56%), (13) (3%), and (14) (7%). Further separation was achieved by column chromatography on silica eluting with diethyl ether-light petroleum. After the elution of hydrocarbons and triphenylphosphine with diethyl ether-light petroleum (5 : 95), the 2 : 1 adducts (1.3 g, 37%) and 1 : 1 adducts (0.41 g, 19%) were obtained with diethyl ether-light petroleum, (25 : 75) and (50 : 50), respectively. A mixture of the major products (11) and (12) was obtained as an oil (Found C, 78.80%; H, 12.17%.  $\text{C}_{12}\text{H}_{22}\text{O}$  requires C, 79.06%; H, 12.16%). Further separation was achieved by preparative g.l.c. (15 ft ×

0.375 in column, 15% Carbowax 20M, 220 °C): (11),  $\tau(\text{CCl}_4)$ , 4.25 (1 H, dd, vinylic), 4.70—5.10 (3 H, m, terminal olefinic and olefinic), 6.55 (1 H, q,  $J$  6 Hz,  $\alpha$ -OH), 7.90—8.20 (2 H, m, allylic), 8.30 (3 H, s, Me), 8.40 (3 H, s, Me), 8.50—8.80 (2 H, m, methylene), 8.85 (1 H, s, OH), 8.95 (3 H, d,  $J$  6 Hz, methyl), and 9.05 (3 H, s, Me);  $m/e$  182 (1%,  $M^+$ ), 95 (32), 82 (100), 69 (89), 68 (42), 67 (47), 55 (32), 45 (37), and 41 (57);  $\nu_{\text{max}}$  3 400s, 3 080s, 3 050s, 2 920s, 1 635w, 1 450m, 1 375m, 1 080s, 1 005w, and 910s  $\text{cm}^{-1}$ ; (12)  $\tau(\text{CCl}_4)$  4.25 (1 H, dd, vinylic), 4.75—5.40 (4 H, m, terminal olefinic), 6.55 (1 H, q,  $J$  6 Hz,  $\alpha$ -OH), 8.05 (2 H, m, allylic), 8.30 (3 H, s, Me), 8.70 (4 H, m, methylene), 8.85 (1 H, s, OH), 8.95 (3 H, d,  $J$  6 Hz, Me), and 9.10 (3 H, s, Me);  $m/e$  82 (100%), 81 (34), 69 (25), 68 (44), 67 (42), 55 (29), 45 (24), and 41 (34);  $\nu_{\text{max}}$  3 600s, 3 070w, 3 000s, 2 935s, 2 970s, 1 660m, 1 450m, 1 370m, 1 080s, 915s, and 885s  $\text{cm}^{-1}$ . Both (11) and (12) were shown by gas chromatography to consist of two diastereoisomers.

[8/846 Received, 8th May, 1978]

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