

## Reactions of a 'Myrcene-Magnesium' Complex with Aldehydes, Ketones, Epoxides, Carbon Dioxide, and Acetonitrile

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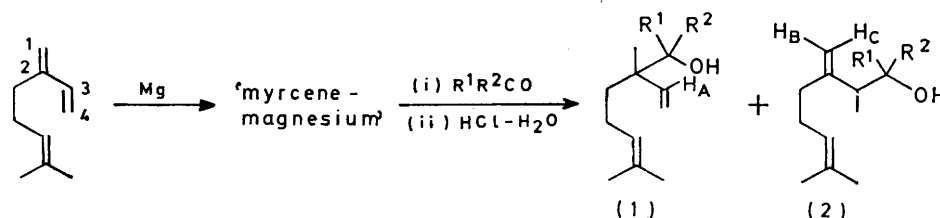
A 'myrcene-magnesium' complex has been prepared by the reaction of myrcene (7-methyl-3-methyleneocta-1,6-diene) with magnesium in the presence of iron(III) chloride and ethyl bromide. Reactions of this complex with aldehydes, ketones, and epoxides yielded mixtures of alcohols by attack at the 2- and 3-positions of the original 1,3-diene unit. Similarly, reactions of the complex with carbon dioxide and acetonitrile gave carboxylic acids and ketones, respectively. The exact nature of these additions is not well understood but steric factors are important in determining product distributions. Some information on the nature of the magnesium complex has been obtained by a study of the hydrocarbons produced by acidic hydrolysis of the 'myrcene-magnesium' complex and the analogous derivatives of *trans,trans*-1,4-diphenylbuta-1,3-diene.

A NUMBER of reports of the reaction of magnesium with acyclic conjugated dienes have appeared.<sup>1</sup> Diene-magnesium complexes have been prepared from reactions of 1,3-dienes with magnesium in the ratio 1 : 1 in the presence of a Lewis acid catalyst such as zinc chloride or iron(III) nitrate in an ether solvent.<sup>2</sup> In this way, complexes of buta-1,3-diene, isoprene, penta-1,3-diene, 1,1-dimethylbuta-1,3-diene, and myrcene were prepared, although no detailed examination of their structures was made. The reaction of 'myrcene-magnesium' with propene oxide followed by decomposition with dilute hydrochloric acid gave 4,9-dimethyl-5-methylenedecan-2-ol. Under similar conditions, the reaction of 'myrcene-magnesium' with acetone yielded a mixture of 2,3,8-trimethyl-4-methylenenonan-2-ol and 2,5-dimethyl-3-(5-methyl-1-methylenehex-4-enyl)hexane-2,5-diol.<sup>2</sup>

acids and ketones. In all cases, these products were the result of 1,2- or 3,4-addition to the 1,3-diene unit of myrcene.

### RESULTS AND DISCUSSION

'Myrcene-magnesium' was prepared by heating myrcene with magnesium in the presence of iron(III) chloride and ethyl bromide in tetrahydrofuran (THF). A series of aldehydes and ketones was added to this solution at room temperature; the major products consisted of the 1 : 1 adducts (1) and (2) (Table 1). Addition to myrcene thus occurred at the 2- and 3-positions of the 1,3-diene unit. The adducts (1) and (2) were distinguished by means of their n.m.r. spectra, which showed a doublet of doublets for H<sub>A</sub> at  $\tau$  4.2 in the former and a singlet at  $\tau$  5.1 for H<sub>B</sub> and H<sub>C</sub> in the latter [ $\tau$  5.2 for (2e) and (2f)].



The preparation of 'isoprene-magnesium' (diene : magnesium 1 : 1) and its reaction with carbonyl compounds have also been examined.<sup>3,4</sup> Hydrolysis of the complex produced, in the presence of a 5% molar quantity of a Lewis acid and a reducing agent, yielded a mixture of C<sub>5</sub>, C<sub>10</sub>, and C<sub>15</sub> hydrocarbons in ratios depending on the nature of these reagents. Reactions of the 'isoprene-magnesium' complex with isobutyraldehyde, n-propionaldehyde, acetone, diethyl ketone, and cyclohexanone yielded complex mixtures of mono- and di-ol products derived from one and two molecules of isoprene. From these results, it was suggested that 'isoprene-magnesium' was a complex mixture of organomagnesium compounds.

The present paper reports the reactions of the 'myrcene-magnesium' complex with aldehydes, ketones, and epoxides to give a series of alcohols, and similar reactions with carbon dioxide and acetonitrile to give carboxylic

Each alcohol contains two chiral centres and appeared as two peaks in g.l.c. analysis. The structures (1a-d)]

TABLE 1

Products from reaction of 'myrcene-magnesium' with aldehydes and ketones

Reagent (R <sup>1</sup> R <sup>2</sup> CO)	Yields of products (%) <sup>a</sup>	
	(1)	(2)
a; R <sup>1</sup> = Me, R <sup>2</sup> = H	23	14
b; R <sup>1</sup> = Et, R <sup>2</sup> = H	9	19
c; R <sup>1</sup> = Pr <sup>n</sup> , R <sup>2</sup> = H	6	23
d; R <sup>1</sup> = Pr <sup>i</sup> , R <sup>2</sup> = H		32
e; R <sup>1</sup> = R <sup>2</sup> = Me	9	31
f; R <sup>1</sup> = Me, R <sup>2</sup> = Et	7	23

<sup>a</sup> Based on 'myrcene-magnesium,' which was formed consistently in ca. 90% yield from myrcene.

were also confirmed by oxidation to the corresponding ketones.

The ratio of adducts (1) and (2) in the reactions with

<sup>1</sup> H. E. Ramsden, U.S.P., 3,354,190/1967; 3,380,179/1968; 3,642,845/1972; 3,711,560/1973.

<sup>2</sup> S. Akutagawa, T. Sakaguchi, and A. Komatsu, Jap.P. 3,770/1971; 15,941/1972; 20,005/1972; 42,824/1972.

<sup>3</sup> M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, *Tetrahedron Letters*, 1970, 3843.

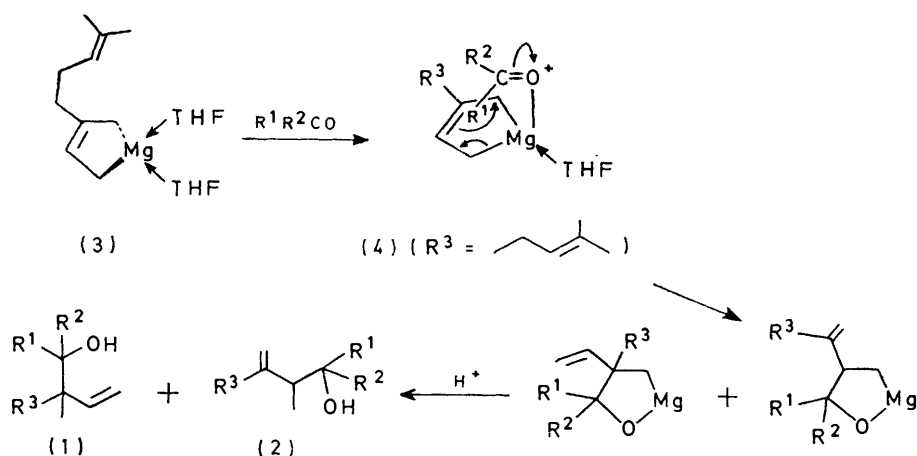
<sup>4</sup> M. Yang, M. Ando, and K. Takase, *Tetrahedron Letters*, 1971, 3529.

the aldehydes depended upon the size of the alkyl groups. Attack at the 2-position was preferred in the case of acetaldehyde but was exclusively at the 3-position for isobutyraldehyde. Although no detailed structural analysis of the intermediate complex has been made, structure (3) is a reasonable representation.<sup>4</sup> In the reaction with carbonyl compounds, initial co-ordination of oxygen to magnesium probably occurs. This might be arranged so that there is overlap between the carbonyl group and the double bond (4). The products can then be envisaged as arising by the route

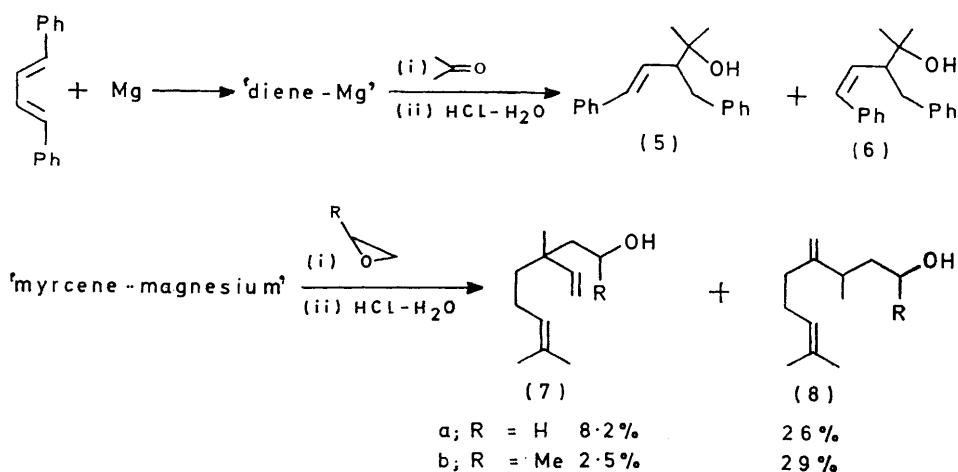
(5) displayed a peak at 970  $\text{cm}^{-1}$  which was absent from the spectrum of (6).

The reaction of 'myrcene-magnesium' with ethylene oxide gave a 1 : 3 mixture of 3,7-dimethyl-3-vinyloct-6-en-1-ol (7a) and 3,8-dimethyl-4-methylenenon-7-en-1-ol (8a); thus addition had taken place at the 2- and 3-positions of the 1,3-diene. A similar reaction with propene oxide yielded a 1 : 10 mixture of 4,8-dimethyl-4-vinylnon-7-en-2-ol (7b) and 4,9-dimethyl-5-methylenedec-8-en-2-ol (8b).

Products were distinguished by their n.m.r. spectra



SCHEME 1



shown in Scheme 1, although an intermolecular process is equally possible. In either of these processes, steric interactions would be important in determining the position of attack.

Such a reaction scheme would involve loss of stereochemistry at C-1 and C-4 of the 1,3-diene; this was confirmed by the reaction of 'trans,trans-1,4-diphenylbuta-1,3-diene-magnesium' with acetone. *trans*-3-Benzyl-2-methyl-5-phenylpent-4-en-2-ol (5) and the *cis*-isomer (6) were formed in 60% yield (based on the magnesium complex). The structures were confirmed by their i.r. spectra; although complete separation was not achieved,

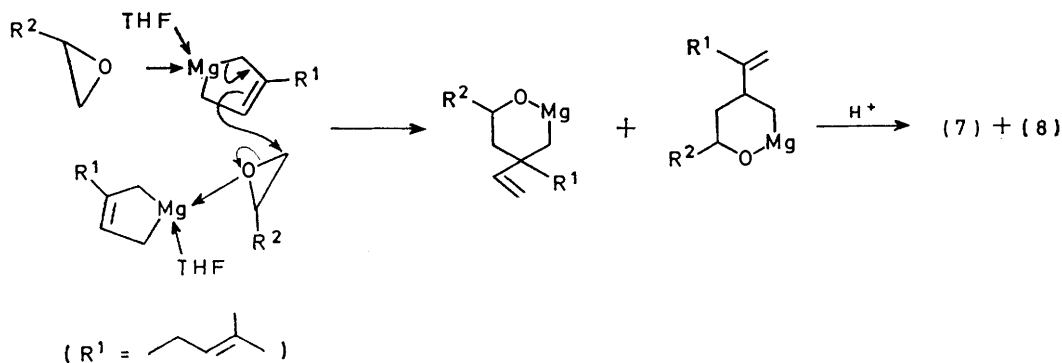
in the same way as before, and the structure (8b) was confirmed by oxidation to the corresponding ketone. Both epoxides attack predominantly at the 3-position, consistent with the importance of steric interactions in these processes which require reaction at  $sp^3$  carbon atoms. An intermolecular reaction (Scheme 2; the arrows exemplify the formation of one of the possible products) is consistent with these observations.

Addition of carbon dioxide to 'myrcene-magnesium' gave 2,7-dimethyl-3-methyleneoct-6-enoic acid (9) and 2-(5-methyl-1-methylenhex-4-enyl)succinic acid (10) in 21 and 7% yields, respectively, and the reaction of the

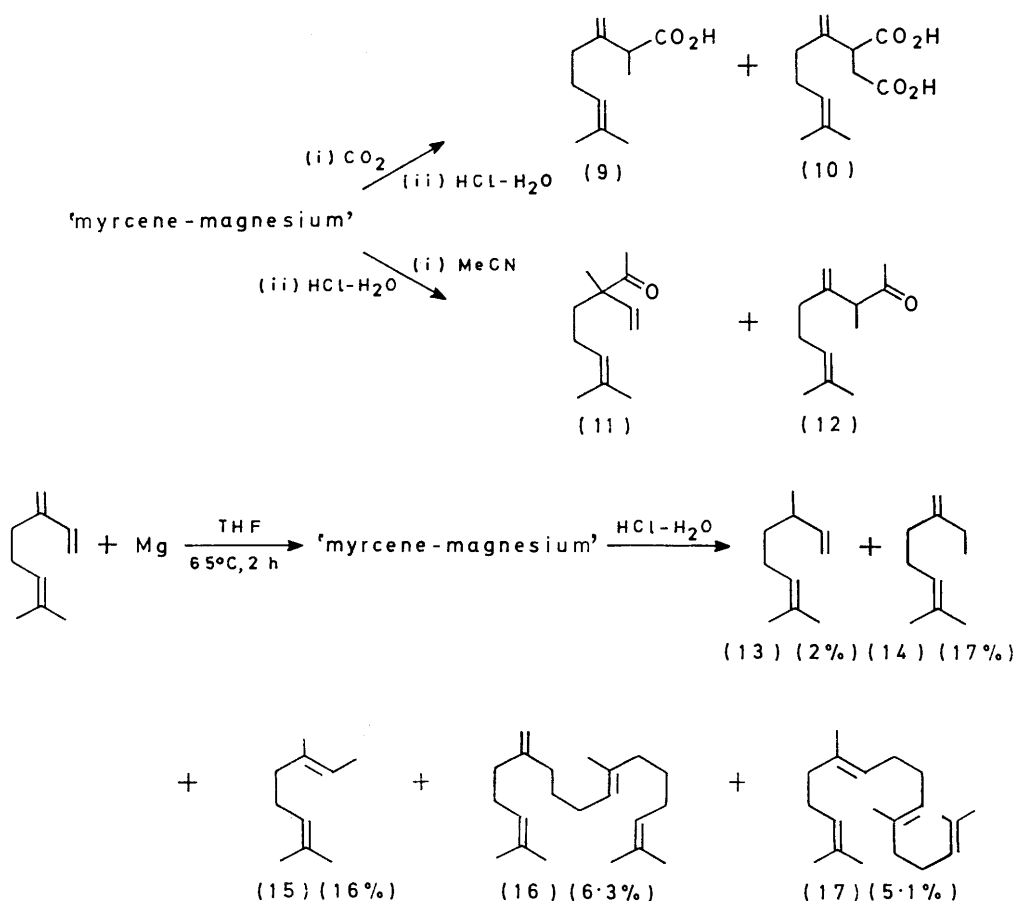
complex with acetonitrile followed by hydrolysis yielded 3,7-dimethyl-3-vinyloct-6-en-2-one (11) (3.4%) and 3,8-dimethyl-4-methylenonon-7-en-2-one (12). The structures (11) and (12) were confirmed by comparison with the identical products prepared by oxidation of (1a) and (2a),

reactions of esters in which cyclisation follows 1,4-addition.<sup>5</sup>

Some information on the initial structure of the 'myrcene-magnesium' complex has been obtained by treatment of the solution with aqueous acid: the mixture of



SCHEME 2



obtained by the reaction of 'myrcene-magnesium' with acetaldehyde.

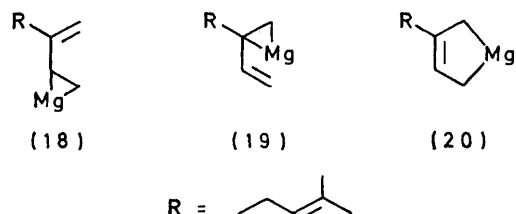
In all these reactions, either 1,2- or 3,4-addition to the 1,3-diene system occurred. In the following paper, we describe reactions of acetyl chloride and acetic anhydride in which a similar process is followed by cyclisation, and

hydrocarbons (13)—(17) was obtained. The C<sub>10</sub> hydrocarbons, which were formed in a total yield of 35% (based on the estimated magnesium complex) were readily distinguished by their n.m.r. spectra. The

<sup>5</sup> R. Baker, R. C. Cookson, and A. D. Saunders, following paper.

stereochemistry of the trisubstituted double bond at C-6 in (15) was assigned by means of the line shape at  $\tau$  8.4 (the signals due to the allylic protons), according to the values given by Faulkner.<sup>6</sup> For compound (16) a characteristic signal at  $\tau$  5.4 for the geminal vinyl protons was observed, and the olefinic protons of (17) displayed a signal at  $\tau$  4.9.

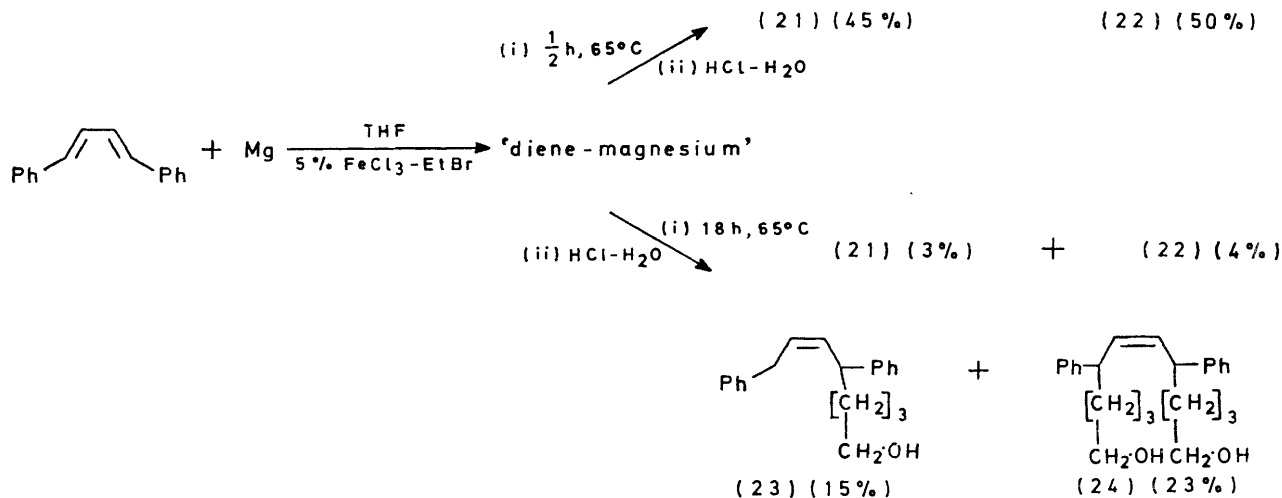
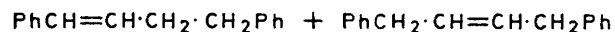
The products are a consequence of 1,2-, 3,4-, and 1,4-protonation. Both types of reaction have been found in the decomposition of 'isoprene-magnesium' by dilute acid.<sup>7</sup> The existence of intermediates of structures (18) and (19) or an equilibrium involving (18), (19), and (20)



cannot be discounted, but the results are consistent with protonation of (20) in any of the four positions.

magnesium' complex. In a series of experiments utilising a range of catalyst/initiators such as  $\text{FeCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{NiBr}_2$ , and  $\text{PdCl}_2$  for formation of the magnesium complex, decomposition with acid gave hydrocarbon mixtures with little variation in product composition except for that anticipated in the case of the longer reaction times for  $\text{PdCl}_2$ .

Predominantly monomeric products, 1,4-diphenylbut-1-ene (21) (45%) and 1,4-diphenylbut-2-ene (22) (50%), were obtained on hydrolysis of the magnesium complex obtained from *trans,trans*-1,4-diphenylbuta-1,3-diene. These two compounds were not separated and their structures were assigned on the basis of an n.m.r. spectrum of the mixture, although the stereochemistry could not be determined. Prolonged heating of the diene-magnesium complex (18 h as compared with 0.5 h), however, led to a mixture of (21) (3%), (22) (4%), 5,8-diphenyloct-6-en-1-ol (23) (15%), and 5,8-diphenyldodec-6-ene-1,12-diol (24) (23%), after hydrolysis with dilute acid. The *cis*-configuration of the double bonds of these 1:1 and 1:2 adducts between the diene and tetrahydrofuran was assigned on the basis of the lack of i.r. absorption at  $970\text{ cm}^{-1}$ . This provides evidence in favour of



Yields of  $\text{C}_{10}$  hydrocarbons were not increased by increasing the amount of magnesium with respect to myrcene. Thus decomposition of 'myrcene-magnesium' prepared from myrcene (0.04 mol) and magnesium (0.06 mol) yielded  $\text{C}_{10}$  hydrocarbons (36%) and  $\text{C}_{20}$  hydrocarbons (13%). The composition of products from 'myrcene-magnesium' did change, however, with reaction time and with heating; increasing reaction times from 2–6 h gave an increasing amount of hydrocarbons consisting of two or more myrcene units. In the reactions with carbonyl compounds and other reagents therefore, the highest yields of 1:1 adducts are to be expected with the shortest reaction time for formation of the 'myrcene-

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

(20) as the most likely structure of the diene-magnesium compounds.

#### EXPERIMENTAL

I.r. and mass spectral data for products in Tables 2 and 3 are available as Supplementary Publications No. SUP 21801 (3 pp.).†

Magnesium powder (B.D.H.) was found by atomic absorption spectroscopy to contain nickel (0.000 1%), copper (0.000 3%), and iron (0.022%).

For all reactions 'myrcene-magnesium' was prepared by heating myrcene (5.66 g.) magnesium (1.0 g), iron(III) chloride (0.34 g, 0.05 mol. equiv. w.r.t. magnesium), and

<sup>6</sup> J. Faulkner, *Synthesis*, 1971, 4, 175.

<sup>7</sup> Y. Nakano, K. Natsukawa, H. Yasuda, and H. Tani, *Tetrahedron Letters*, 1972, 2833.

ethyl bromide (0.2 ml) in tetrahydrofuran (40 ml) for 2 h at 65 °C, which gave *ca.* 90% conversion into the complex. This conversion was calculated on the basis of the diene consumed; since no account was taken of thermal polymerisation of the diene, it must represent a maximum value.

*Reactions with Aldehydes and Ketones.*—'Myrcene-magnesium' was cooled to room temperature and the aldehyde (0.04 mol) was added dropwise at such a rate that the solution did not boil. The complex was stirred for 0.5 h, then a stoichiometric quantity of dilute hydrochloric acid was added dropwise. The solution was stirred until clear and extracted with ether. The dried extract was evaporated and the residue distilled at reduced pressure to give fractions containing unchanged myrcene and the myrcene-aldehyde adducts. The second fraction, containing the adducts, was analysed by g.l.c. (Pye 104; carrier gas N<sub>2</sub>, at 60 ml min<sup>-1</sup>; 10 ft 15% PPGA; 170 °C), and between two and four isomeric products were detected. Separation was achieved by

*Reactions with Ethylene and Propene Oxides.*—'Myrcene-magnesium' was cooled to room temperature and the epoxide (0.04 mole) was added dropwise at such a rate that the solution did not boil. The complex was stirred for 0.5 h before decomposition; the dried ethereal extract was evaporated and the residue distilled at reduced pressure to give two fractions. In both cases a small amount of unchanged myrcene was recovered, followed by the fraction containing the alcohol products. G.l.c. analysis (10 ft 15% PPGA; 170 °C) indicated two products from ethylene oxide (*t<sub>R</sub>* 15.8 and 16.7 min) and three from propene oxide (11.3, 12.0, and 12.7 min). The products were isolated by chromatography [alcohol mixture (1 g) on silica gel (50 g)] with 3% ether-petroleum in the first case and 10% ether-petroleum in the second as eluant. The products from ethylene oxide were (7a) and (8a) (2.9 g, 36%), boiling range 100–120° at 5 mmHg, and from propene oxide (7b) and (8b) (2.8 g, 32%), boiling range 100–120° at 5 mmHg.

TABLE 2

Reagent	Products	<sup>1</sup> H N.m.r. data of products from reactions of 'myrcene-magnesium' with aldehydes and ketones τ(CCl <sub>4</sub> ) (J in Hz)
MeCHO	3,7-Dimethyl-3-vinyloct-6-en-2-ol (1a)	8.9 (6 H, 2 × d, J <sub>1</sub> = J <sub>2</sub> = 6.7), 8.3 (6 H, d), 7.9 (5 H, br), 6.3 (1 H, m), 5.1 (2 H, s), 4.9 (1 H, br), 8.7 (OH)
	3,8-Dimethyl-4-methylenenon-7-en-2-ol (2a)	8.9 (3 H, s), 8.9 (3 H, d, J 6.7), 8.7 (2 H, m), 8.4 (6 H, d), * 7.9 (2 H, br), 6.3 (1 H, q, J 6.7), 5.2 (1 H, m), 4.9 (2 H, m), 4.2 (1 H, dd, J <sub>cis</sub> 12.0, J <sub>trans</sub> 18.0), 8.8 (OH)
EtCHO	4,8-Dimethyl-4-vinylnon-7-en-3-ol (1b)	9.05 (2 H, t, J 6.0), 8.95 (3 H, s), 8.5 (4 H, m), 8.4 (6 H, d), * 8.0 (2 H, m), 6.7 (1 H, t, J 6.0), 5.2 (1 H, m), 5.0 (2 H, m), 4.2 (1 H, dd, J <sub>cis</sub> 10.7, J <sub>trans</sub> 18.0), 8.05 (OH)
	4,9-Dimethyl-5-methylenedec-8-en-3-ol (2b)	9.05 (3 H, t, J 6.0 Hz), 8.95 (3 H, d, J 6.0), 8.7 (2 H, m), 8.4 (6 H, d), * 8.0 (5 H, br), 6.7 (1 H, m), 5.2 (2 H, s), 4.9 (1 H, br), 8.85 (OH)
Pr <sup>n</sup> CHO	5,9-Dimethyl-5-vinyldec-8-en-4-ol (1c)	9.1 (3 H, t, J 6.0), 9.05 (3 H, s), 8.7 (6 H, m), 8.4 (6 H, d), * 8.0 (2 H, br), 6.7 (1 H, t, J 6.0), 5.2 (1 H, m), 5.0 (2 H, m), 4.3 (1 H, dd, J <sub>cis</sub> 11.3, J <sub>trans</sub> 18.0), 8.9 (OH)
	5,10-Dimethyl-6-methyleneundec-9-en-4-ol (2c)	9.0 (3 H, t, J 6.0), 8.9 (3 H, d, J 6.0), 8.6 (4 H, m), 8.35 (6 H, d), * 7.95 (4 H, d), 7.7 (1 H, m), 6.6 (1 H, m), 5.2 (2 H, s), 4.9 (1 H, s), 8.85 (OH)
Pr <sup>i</sup> CHO	2,4,9-Trimethyl-5-methylenedec-8-en-3-ol (2d)	9.1 (9 H, m), 8.4 (7 H, d), * 8.0 (4 H, br), 7.85 (1 H, m), 6.95 (1 H, dd), 5.2 (2 H, s), 4.9 (1 H, br), 8.8 (OH)
Me <sub>2</sub> CO	2,3,7-Trimethyl-3-vinyloct-6-en-2-ol (1e)	9.1 (3 H, s), 8.98 (6 H, s), 8.7 (2 H, t, J 4.0), 8.4 (6 H, d), * 8.2 (2 H, m), 4.9 (3 H, m), 4.2 (1 H, d, J <sub>cis</sub> 12.0, J <sub>trans</sub> 18.0), 8.6 (OH)
	2,3,8-Trimethyl-4-methylenenon-7-en-2-ol (2e)	8.95 (3 H, d, J 7.2), 8.86 (6 H, s), 8.4 (6 H, d), * 7.95 (5 H, m), 5.2 (2 H, d), 4.9 (1 H, br), 8.25 (OH)
MeCOEt	3,4,8-Trimethyl-4-vinylnon-7-en-3-ol (1f)	9.16 (3 H, t, J 8.0), 9.04 (3 H, s), 9.0 (3 H, s), 8.6 (4 H, m), 8.4 (6 H, d), 8.0 (2 H, t, J 8.0), 5.0 (3 H, m), 4.2 (1 H, dd, J <sub>cis</sub> 10.0, J <sub>trans</sub> 18.0), 8.5 (OH)
	3,4,9-Trimethyl-5-methylenedec-8-en-3-ol (2f)	9.18 (3 H, t, J 7.0), 9.03 (3 H, d, J 6.4), 9.0 (3 H, s), 8.6 (2 H, q, J 7.0), 8.4 (6 H, d), * 8.0 (OH)

\* Two peaks, separation *ca.* 4 Hz.

column chromatography with the product (1.0 g) on silica gel (5% ether-petroleum as eluant; fractions of 50 ml). No attempt was made to isolate the diastereoisomers separately, and preparative g.l.c. (Pye 105; N<sub>2</sub> at 225 ml min<sup>-1</sup>; 30 ft 15% PPGA; 170 °C) was required for separation of the products from reactions with acetaldehyde and acetone.

Conversion into the 'myrcene-magnesium' complex was *ca.* 87%, and yields of the aldehyde and ketone adducts are summarised in Table 1; n.m.r. characteristics are detailed in Table 2.

The b.p. ranges of the adducts and analytical g.l.c. details are as follows: (1a) and (2a), 100–130° at 5 mmHg, four peaks (*t<sub>R</sub>* 6.0, 6.5, 7.5, and 7.9 min); (1b) and (2b), 100–130° at 5 mmHg, three peaks (9.0, 10.5, and 11.0 min); (1c) and (2c), 120–140° at 5 mmHg, three peaks (12.0, 14.5, and 15.0 min); (1d) and (2d), 120–150° at 5 mmHg, one peak (10.5 min); (1e) and (2e), 100–120° at 5 mmHg, two peaks (8.0 and 9.6 min); (1f) and (2f), 105–125° at 5 mmHg, three peaks (10.4, 11.4, and 13.7 min).

*Reaction with Carbon Dioxide.*—'Myrcene-magnesium' was cooled to -25 °C and powdered solid carbon dioxide (1.8 g) was added slowly. The complex was allowed to warm to room temperature and stirred for 15 min before decomposition. The ethereal extract contained acids (*v<sub>max</sub>* 2 800 and 1 700) which were separated by treatment with aqueous sodium carbonate, followed by acidification of the aqueous layer and extraction with ether. Analysis by g.l.c. (5 ft 3% SE 30; 200 °C) indicated the presence of two products, (9) and (10). Separation was achieved by chromatography [mixture (2 g) on silica gel (60 g)] with 10% ether-petroleum as eluant [20% ether for the elution of (1)]. The product (9) (25% yield) had m.p. 101–102°; (10) was a yellow oil.

*Reaction with Acetonitrile.*—'Myrcene-magnesium' was cooled to room temperature and acetonitrile (1.7 g) was added dropwise at such a rate that the solution did not boil. The complex was stirred for 15 min before decomposition, extraction with ether, and distillation at reduced pressure to yield unchanged myrcene and a mixture of ketones (18%

yield), boiling range 90—120° at 5 mmHg. The ketones (11) and (12) (0.5 g), separated on silica gel (25 g) with 1% ether-petroleum ether as eluant, were obtained as oils.

*Decomposition of 'Myrcene-Magnesium' with Dilute Acid.*—The complex was cooled to -10 °C and a stoichiometric quantity of dilute hydrochloric acid was added dropwise. The solution was allowed to warm to room temperature and extracted with ether. The dried extract was evaporated and the residue distilled at reduced pressure to yield two fractions with boiling ranges 40—60 and 120—150° at 5 mmHg. G.l.c. analysis of fraction (1) (10 ft 15% PPGA; 100 °C) showed three peaks ( $t_R$  2.4, 3.2, and 3.6 min) and fraction (2) (at 170 °C) two peaks (25.9 and 30 min). Products were isolated by preparative g.l.c. to yield the hydrocarbons (13)—(16) as oils. The n.m.r. spectrum of (16) showed  $\tau$  (CCl<sub>4</sub>) 8.65 (2 H, m), 8.40 (15 H, d), 8.05br (12 H), 5.4 (2 H, s), and 5.0br (3 H). Complete separation of (17)

(neat) 3 400, 3 050, 3 020, 2 970, 2 920, 2 880, 1 605, 1 505, 1 465, 1 395, 1 160, 1 130, 760, and 710 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.85 (6 H, d), 6.5 (3 H, m), 4.0 (1 H, d,  $J$  6.0 Hz), 3.3 (1 H, d,  $J$  6.0 Hz), 2.9 (10 H, m), and 7.7 (OH).

*Decomposition of 'trans,trans-1,4-Diphenylbuta-1,3-diene-Magnesium'.*—The complex was prepared as described above and heated at 65 °C for 0.5 h before decomposition. Chromatography of the crude product on silica gel and elution with 10% ether-petroleum gave a white solid consisting of a mixture of olefins (21) and (22) (95%) in the ratio 10 : 9 as indicated by g.l.c. (5 ft 2½% SE 30; 170 °C),  $v_{max}$  (neat), 3 040, 3 010, 2 910, 2 850, 1 605, 1 500, 1 460, 1 080, 1 040, 980, 750, and 700 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 7.4 (m), 6.7 (m), 4.4 (m), 3.7 (m), and 2.9 (m).

Heating the complex for 18 h before decomposition gave a 96.0% conversion into the 'diene-magnesium' derivative. Part of the crude product (1 g) was chromatographed on

TABLE 3

<sup>1</sup>H N.m.r. data of products from reactions of 'myrcene-magnesium' with ethylene oxide, propene oxide, acetonitrile, and carbon dioxide

Reagents	Products	$\tau$ (CCl <sub>4</sub> ) ( $J$ in Hz)
Ethylene oxide	3,7-Dimethyl-3-vinyl-oct-6-en-1-ol (7a)	9.07 (3 H, s), 8.7 (2 H, q, $J$ 8.0), 8.45 (8 H, t), 8.05 (2 H, br), 6.6 (2 H, t, $J$ 6.0), 5.1 (3 H, m), 4.3 (1 H, dd, $J_{cis}$ 11.0, $J_{trans}$ 17.0), 6.75 (OH)
	3,8-Dimethyl-4-methylenenon-7-en-1-ol (8a)	9.02 (3 H, d, $J$ 7.4), 8.4 (8 H, t), 8.04 (5 H, br), 6.6 (2 H, t, $J$ 6.0), 5.4 (2 H, d), 5.0 (1 H, br), 6.4 (OH)
Propene oxide	4,8-Dimethyl-4-vinylnon-7-en-2-ol (7b)	8.92 (3 H, s), 8.9 (3 H, d, $J$ 6.0), 8.6 (2 H, t, $J$ 4.0), 8.35 (8 H, d), 8.0 (2 H, br), 6.1 (1 H, m), 5.0 (3 H, m), 4.0 (1 H, dd, $J_{cis}$ 9.0, $J_{trans}$ 15.0), 8.7 (OH)
	4,9-Dimethyl-5-methylenedec-8-en-2-ol (8b)	9.03 (3 H, d, $J$ 7.6), 8.94 (3 H, d, $J$ 7.0), 8.6 (2 H, m), 8.4 (6 H, d), * 8.0 (5 H, br), 6.4 (1 H, m), 5.35 (2 H, d), 5.0 (1 H, br), 7.15 (OH)
CO <sub>2</sub>	2,7-Dimethyl-3-methyleneoct-6-enoic acid (9)	8.75 (3 H, d, $J$ 7.0), 8.4 (6 H, d), * 7.95 (4 H, t), 7.0 (1 H, q, $J$ 7.0), 5.15 (2 H, d), 5.03 (1 H, br), -0.48 (CO <sub>2</sub> H)
	2-(5-Methyl-1-methylenehex-4-enyl)-succinic acid (10)	8.4 (6 H, d), * 7.95 (4 H, br), 7.1 (2 H, d, $J$ 7.0), 6.6 (1 H, t, $J$ 7.0), 5.15 (3 H, br), -0.62 (CO <sub>2</sub> H)
CH <sub>3</sub> CN	3,7-Dimethyl-3-vinyloct-6-en-2-one (11)	8.9 (3 H, s), 8.6 (2 H, m), 8.4 (6 H, d), * 8.05 (3 H, s), 7.9 (2 H, br), 5.0 (3 H, m), 4.2 (1 H, dd, $J_{cis}$ 8.7, $J_{trans}$ 18.0)
	3,8-Dimethyl-4-methylenenon-7-en-2-one (12)	8.9 (3 H, d, $J$ 6.7), 8.4 (6 H, d), 8.05 (3 H, s), 7.9 (4 H, br), 6.95 (1 H, q, $J$ 6.7), 5.15 (2 H, s), 4.95 (1 H, br)

\* Two peaks, separation *ca.* 4 Hz.

was not achieved, and it was identified on the basis of the n.m.r. spectrum of a mixture of (16) and (17) [ $\tau$  (CCl<sub>4</sub>) 5.8 (18 H, d), 8.0br (12 H), and 4.9br (4 H)].

*Reactions of 'trans,trans-1,4-Diphenylbuta-1,3-diene-Magnesium' with Acetone.*—The complex was prepared by heating *trans,trans*-1,4-diphenylbuta-1,3-diene (8.6 g) with magnesium (1.0 g) and iron(III) chloride (0.34 g) in tetrahydrofuran (40 ml) for 1 h. Acetone was added at room temperature and the solution stirred for 1.5 h before decomposition with dilute acid. The dried ethereal extract was evaporated to yield crude product (12.6 g). Separation of this product (2.0 g) on silica gel with 5% ether-petroleum as eluant gave the alcohols (5), an oil,  $m/e$  266, 249, 248, 233, 208, 157, 117, 91, 77, and 47;  $v_{max}$  (neat), 3 400, 3 040, 3 000, 2 970, 2 920, 2 860, 1 605, 1 505, 1 485, 1 380, 1 165, 1 130, 975, 755, and 705 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.95br (6 H), 6.7 (3 H, m), 3.4br (2 H), 3.0 (10 H, m), and 8.4 (OH); and (6), an oil,  $m/e$  266, 249, 248, 233, 208, 205, 157, 117, 91, 77, and 47;  $v_{max}$

silica gel (50 g). A mixture of (21) and (22) (0.09 g) was eluted with 1% ether-petroleum ether, the alcohol (23) (0.18 g) with 30% ether-petroleum, and the alcohol (24) (0.42 g) with 70% ether-petroleum. Both compounds (23) and (24) were obtained as oils: (23) showed  $m/e$  280, 262, 245, 207, 189, 171, 145, 129, 91, 77, 65, 55, 43, and 41,  $v_{max}$  (neat) 3 400, 3 010, 2 920, 2 800, 1 600, 1 500, 1 460, 1 075, 1 030, 975, 800, 760, and 700 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.5 (6 H, m), 6.6 (5 H, m), 4.5 (2 H, m), 2.9br (10 H), and 7.4 (OH); (24) showed  $m/e$  352, 334, 279, 261, 205, 191, 181, 145, 129, 118, 116, 105, 91, 55, 43, and 41;  $v_{max}$  (neat) 3 350, 3 030, 2 920, 2 850, 1 600, 1 500, 1 460, 1 060, 1 035, 980, 795, 760, and 700 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.5 (12 H, m), 6.6 (6 H, m), 4.5br (2 H), 2.9 (10 H, t), and 6.65 (OH).

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