Preparation and Stereochemistry of Some 1,1-Disubstituted Buta-1,3-dienes

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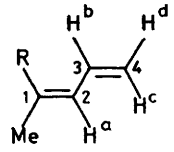
The preparation of five (*E*)- and five (*Z*)-1,1-disubstituted buta-1,3-dienes is described and their stereochemistry assigned. The effect of the *Z*–*E* isomerism on the chemical shifts in the ^{13}C and ^{1}H n.m.r. spectra is discussed.

In connection with our studies on the ring-opening reactions of 3,3-disubstituted cyclobutenes,[1] we had need of some authentic samples of 1,1-disubstituted butadienes † of known configuration. While a number of compounds of this type are recorded in the literature [2-5] the stereochemistry has been assigned in only a few cases.[3] Of the ten dienes that we required [(1 a—e) and (2a—e)], only (2a) [4] and (2d) [5] have been reported, but without any stereochemical assignment. An early report of the preparation of (2e) [6] has been shown to be



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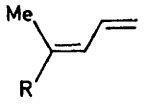
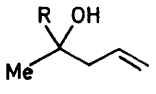


(2)

a; R = Pr^n
b; R = Pr^i
c; R = Bu^t
d; R = cyclopropyl
e; R = Ph
f; R = Et



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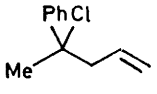
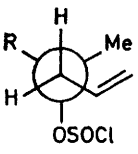


(6)

erroneous,[7] and the only subsequent mention does not report any physical constants.[8] We here report the preparation and stereochemical assignments of the five (Z)-(1a—e) and five (E)-1,3-butadienes (2a—e).

Synthesis.—One of the major problems in the synthesis of terminal alkadienes, normally glossed over, is their ease of polymerisation, and the majority of elimination reactions on suitable allyl and homoallyl precursors leads to low yields as a result of this subsequent reaction of the desired product.

We find that the homoallylic alcohols (3a—d), readily



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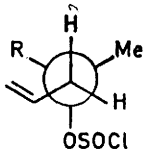
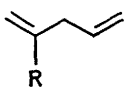
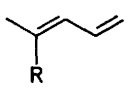
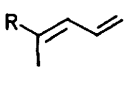
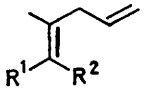


(5)

a; R = Pr^n
b; R = Pr^i
c; R = Bu^t
d; R = cyclopropyl
e; R = Ph
f; R = Et

prepared in high yield from the reaction of allylmagnesium bromide on the requisite methyl ketone, can be dehydrated in yields of *ca.* 50% using thionyl chloride in pyridine at 0 °C, followed by immediate extraction with ether. The method is essentially that of Lomas,[9] but the use of his conditions leads to extensive polymerisation and yields of *ca.* 5%. Compared to alternative syntheses,[10] this route is quick, simple, and gives acceptable overall yields from readily available precursors. In all cases, elimination gave a mixture of 1,3- and 1.4-dienes corresponding to the loss of any available hydrogen β to the hydroxy-group, and the composition of each mixture is shown in the Table.

Diene product composition from dehydration of homoallylic alcohols (3)

R in (3)		 (1)	 (2)		Yield of alkadienes (%)	Calc./*Z* : *E* ratio [e]
(a) n-propyl	5	22 (40) [a]	33 (60)	40 [b]	52	36 : 64
(b) isopropyl	21	14 (36)	25 (64)	40 [c]	50	36 : 64
(c) t-butyl	36	0 (0)	64 (100)		67	0.5 : 99.5
(d) cyclopropyl	25	38 (51)	37 (49)	0	29	*f*
(e) phenyl [d]	45	12 (22)	43 (78)		85	24 : 76

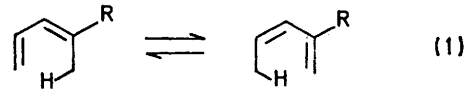
[a] Figures in brackets show the ratio of (1) : (2). [b] R^1 = Et, R^2 = H and R^1 = H, R^2 = Et. Stereochemistries not assigned. [c] R^1 = R^2 = Me. [d] From pyrolysis of chloride (6), see text. [e] Using cyclohexane A-values, [12] see text. [f] No A-value available.

The ratio of (*E*)- to (*Z*)-1,3-diene formed in the dehydration shows the favoured production of the thermodynamically more stable *E*-isomer (2), which is to be expected if elimination takes place in an antiperiplanar fashion and R is larger than methyl, as can be seen from the Newman diagrams (4) and (5). This *E* : *Z* ratio is

† All the 1,3-dienes in this paper are of the 4-substituted penta-1,3-diene type (1). Correct nomenclature normally includes the substituent R in the longest chain, the compound then being classed as a hexadiene, heptadiene, etc. In order to facilitate the discussion they will be referred to as 1,1-disubstituted butadienes.

close to that calculated if the relative steric effect of the group R compared to methyl is *ca.* 75% of the equatorial–axial conformational free-energy difference (A-value) for the group on a cyclohexane.[11] The calculated values are given in the Table. The close agreement between the calculated and observed ratios would tend to confirm that the elimination occurs by a concerted and antiperiplanar route. For R = t-butyl, this steric effect is such that none of the *Z*-diene (1c) is formed. It was therefore prepared by photosensitised isomerisation of the *E*-isomer (2c) which gave a binary mixture of (1c) and (2c), containing 41% of the former.

When (3e) was treated with $SOCl_2$–pyridine under the same conditions as the alkyl compounds, considerable



(1)

(2) (7)

polymerisation occurred and only the homoallylic chloride (6) was isolated. Pyrolytic elimination of HCl from (6) at 190 °C in the injection block of the preparative g.l.c. gave the mixture of dienes shown in the Table.

Pure samples of the (*Z*)- and (*E*)-1,3-dienes were obtained by careful preparative g.l.c. for, although the 1,3-dienes were readily separable from their 1,4-isomers, separation of the geometric isomers required very careful choice of column and conditions. Only in the case of (1c) was a pure sample not obtained and the spectral data recorded were derived from an enriched mixture containing the *E*-isomer (2c) as impurity.

Stereochemical Assignment.—The stereochemistry of the isomers (1) and (2) was determined by a combination of the use of the [1,5] hydrogen shift and ^{13}C and ^1H n.m.r. spectrometry.

[1,5] *Hydrogen shift.* Substituted 1,3-dienes that can adopt the required *s-cis* conformation and have a suitably placed hydrogen can undergo a [1,5] sigmatropic shift of hydrogen from one end of the diene system to the other [equation (1)].[12,13] When the group R does not have an available hydrogen, this provides a ready means for distinguishing between (1) and (2), for only the *E*-diene (2) will isomerise. Typically the [1,5] hydrogen shift has an activation energy of 134 kJ mol^{-1} and takes place rapidly at temperatures of 240—300 °C.[13]

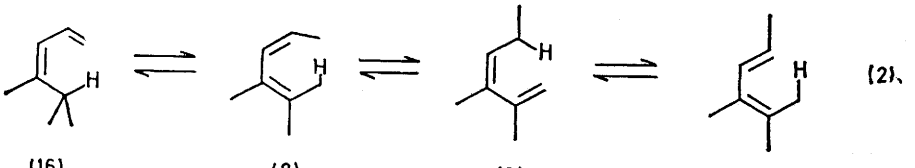
Pyrolysis of the diene obtained by dehydration of (3c; R = Bu^t) at 240 °C readily gave an isomer identified as (7; R = Bu^t) (^1H n.m.r.) and hence the original diene can be assigned the *E*-configuration shown in the Table.

Separation by g.l.c. of the 1,3-dienes obtained from dehydration of (3b) yielded one of shorter retention time (minor) and one of longer retention time (major). Pyrolysis of the former for a short time at 250 °C gave a single product (8), while pyrolysis for a longer time gave three products as a result of the further [1,5] hydrogen shifts shown in equation (2). The structures of (8)—(10) were identified by ^1H n.m.r. spectroscopy after g.l.c. of the mixture. This enables the minor component to be assigned the *Z*-stereochemistry (1b). The major component was more resistant to pyrolysis, but, after 2.5 h at 295 °C, was converted (18%) into a single isomeric diene (7; R = Pr^i) as expected for the *E*-diene (2b).

For the phenyl-substituted 1,3-diene (as for R = Bu^t) only the *E*-isomer (2e) can undergo the [1,5] hydrogen shift, and the isomer of longer retention time on g.l.c. proved to be readily isomerised at 240 °C to (7; R = Ph), while the isomer of shorter retention time was resistant to pyrolytic change even at 300 °C, as expected for the *Z*-isomer (1e).

Although this method could be applied to the n-propyldienes (1a) and (2a), the subsequent [1,5] shifts which the first product may undergo [as with the isopropyl compound (1b)] makes the technique unattractive and it was not attempted.

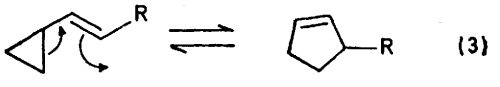
This method could not, however, be applied to the identification of the isomers (1d) and (2d; R = cyclopropyl) due to the intervention of the vinylcyclopropane–cyclopentene rearrangement, equation (3).[14] Although not occurring in vinylcyclopropane itself (11; R = H) until *ca.* 340 °C, it is facilitated by further vinyl



(2)

(16) (8) (9) (10)

substitution and (*E*)-cyclopropylbuta-1,3-diene (11; R = vinyl) rearranges at temperatures down to 270 °C.[15] At this temperature, the rearrangement of equation (3) would compete with the [1,5] hydrogen shift and interfere with the stereochemical assignment, since both



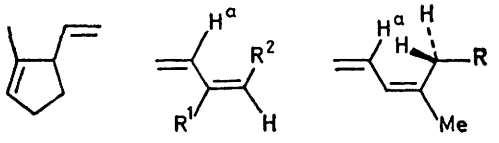
(3)

(11)

cyclopropylpentadienes (1d) and (2d) would yield the same vinylcyclopentene (12). Indeed pyrolysis of either (1d) or (2d) gave only a single identical product, not identified, but presumably (12).

^{13}C *N.m.r. spectra.* Broad band, proton-decoupled, Fourier transform ^{13}C n.m.r. spectra of the eight dienes

(1a—d) and (2a—d) were recorded in $CDCl_3$. Off-resonance decoupling allowed the signals to be assigned. (Detailed ^{13}C and ^1H n.m.r. assigments are available as Supplementary Publication No. SUP 22759 *). A study of the data for the *Z*- and *E*-isomers of the isopropyl- and t-butyl-dienes, where the stereochemistry had already been assigned, enabled the following conclusions to be drawn concerning the dependence of chemical shift on



(12) (13) (14)

stereochemistry. The atoms showing the largest and most consistent dependence on the *Z*—*E* isomerism are C-3 of the trisubstituted double bond and the α-carbon atoms of the alkyl substituents (including the methyl group). The largest differential shielding is shown by C-3, where the *Z*-isomers resonate at lower field (125—126 p.p.m.) than do the *E*-ones (122—123 p.p.m.). Similarly the methyl group of the *E*-isomer resonates at higher field than that of the *Z*-isomer, while for the R group, it is the α-carbon of the *Z*-isomer which shows the higher field resonance. Thus in each case it is the α-carbon which is *cis* to the vinyl group which is upfield.

As a general rule, the ^{13}C n.m.r. shifts of carbon atoms in spatially crowded alkyl groups occur at higher field than those of similar unperturbed carbons.[16] This has been attributed to 1,4-non-bonded interactions causing partial polarisation of the C–H bonds and hence shielding changes at carbon.[17] The magnitude of this differential shielding then depends on the number of hydrogen atoms attached to the particular carbon and its relative spatial orientation with respect to the rest of the molecule.

A detailed study of the ^{13}C n.m.r. spectra of di- and tri-substituted alkenes has been made by Haan and van de Ven,[18] and results have also been reported by Dorman [19] and by Lippmaa.[20] In all cases the α-carbon atoms of the *Z*-isomers have been found to be at higher fields, with consistent values for the differential shielding between the two stereoisomers. In trisubstituted alkenes these values are rather larger than in disubstituted ones, probably due to the steric interaction between the geminal substituents. Results on penta-1,3-diene and the hexa-2,4-dienes have shown that conjugation of the double bond has relatively little effect on the alkene part of the ^{13}C n.m.r. spectra and that the differential shielding of the α-carbon atom is the best probe for stereochemistry with *cis–trans* differences of 4 to 5 p.p.m.[18]

Our results on the trisubstituted double-bond of the alkadienes are in good agreement with these conclusions, although for R = Bu^t the shift of the methyl group is rather smaller than for the other compounds, presumably due to the large geminal interaction in both isomers. Thus even in the *Z*-isomer (1c) the methyl resonance occurs 4 p.p.m. upfield from that for the isopropyl compound (1b). The α-carbon of the t-butyl group is almost unaffected by the change in stereochemistry due to the absence of hydrogen atoms directly attached to it, although again the *Z*-isomer resonates at higher field.

Separation of the two 1,3-dienes obtained by dehydration of (3d) gave, in nearly equal amounts, one isomer of shorter and one of longer retention time on g.l.c. The ^{13}C n.m.r. spectrum of the former corresponded with that of the other *E*-dienes, with C-3 resonating at 123.97 p.p.m. and with the methyl group at higher field by 5 p.p.m. than in the other isomer. The stereochemistries were therefore assigned as *E*- and *Z*- respectively, to the 1,3-dienes of short and long retention time.

Similarly for the n-propyldienes (1a) and (2a), the *E*-stereochemistry was assigned to that isomer showing the higher field resonance both for C-3 and for the vinylic methyl group: 125.58 and 16.51 p.p.m. compared to 126.42 and 23.71 p.p.m.

^1H *N.m.r. spectra.* With the identification of the dienes (1a—d) and (2a—d) changes in the ^1H n.m.r. spectra could be correlated with the geometrical differences. Details of the ^1H n.m.r. spectra of these dienes together with those of (1f) and (2f), identified by Frey and Solly,[3] are contained in SUP 22759.

Previous ^1H n.m.r. studies [21,22] on the stereochemistry of di- and tri-substituted alkenes have reached conclusions that are qualitatively similar to those from the more recent ^{13}C n.m.r. work.[18] In general, spatially crowded protons are deshielded, but the differences are rather small and can be masked by overlapping peaks. For disubstituted alkenes, the methine proton of an isopropyl group is deshielded by *ca.* 0.3 p.p.m.[23] and in trisubstituted alkenes this increases to *ca.* 0.6 p.p.m.[24] However for methylene and methyl protons these shifts are only *ca.* 0.1 p.p.m. to higher and lower field, respectively,[22] and are therefore less reliable for stereochemical assignment. Originally it was suggested that the effect was due to the anisotropy of the double-bond, [23,24] with the relevant proton being held within the deshielding region by conformational effects, but more recent results on the vinyl proton H^a of the dienes (13) indicate that steric compression is a more likely explanation.[25] Our own results tend to favour the latter explanation, for the vinyl proton H^a is at τ 3.53—3.56 in all the *E*-isomers (1) and is shifted downfield in the *Z*-isomers (2b—d). The largest shift is observed when R = Bu^t (0.31 p.p.m.), with smaller shifts for R = cyclopropyl (0.24) and isopropyl (0.06 p.p.m.), while when R = Et or Pr^n there is no difference. This indicates that there is a marked preference for the conformation (14; R = Me or Et) where for H^a the difference between the *E*- and *Z*-isomers (14; R = H) is minimal.

For the allylic protons, our observations are in accord with the previous results on simple alkenes,[22-24] the *Z*-isomers (1a) and (1f) having the allylic methylene *ca.*

* For details of the Supplementary Publications scheme, see Notices to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

0.10 p.p.m. to lower field than for (2a) and (2f), with a larger difference for the methine proton of (1b) compared to (2b). However, in contradistinction to the previous results on trisubstituted alkenes,[22] we observe that when a methyl is *cis* to the vinyl group (*E*-isomers), it also experiences a small (0.03 p.p.m.) downfield shift, except when R = Bu^t.

G.l.c. With the exception of the cyclopropyl compounds (1d) and (2d), we find that the order of elution of the *Z*–*E*-isomeric 1,3-dienes is always such that the *Z*-isomer (1) has the shorter retention time, and this correlation was used to assign tentatively the configurations of the 1,4-dienes obtained by dehydration of (3a).

EXPERIMENTAL

I.r. and u.v. spectra were recorded on Unicam SP200 and SP800 spectrometers. ^{1}H N.m.r. spectra were measured at 60 MHz on a Perkin-Elmer R12 spectrometer and at 100 MHz on a Varian Associates HA 100 instrument, with tetramethylsilane as internal reference. ^{13}C N.m.r. spectra were measured either on a Bruker HFX 90E or on a Varian Associates XL100 instrument. Mass spectra were measured on an AEI MS12 spectrometer. Analytical g.l.c. was carried out on a Perkin-Elmer F11 chromatograph equipped with a flame-ionisation detector. Peak areas were recorded using a Disc series 200 ball-and-disc integrator. Calibration factors were determined by standard techniques. Preparative g.l.c. was done on a Varian Aerograph 1700 Autoprep instrument, fitted with a thermal conductivity detector, and using hydrogen as carrier gas. The columns used for g.l.c. were: Column A, 2 m × 3 mm, 10% Carbowax 20 M on Chromosorb W; Column B, 2 m × 3 mm, 20% 1.3 DCEP on Phasesep P; Column C, 4 m × 3 mm, 15% PPG on Chromosorb W; Column D, 4 m × 3 mm, 15% PPGA on Chromosorb W; Column E, 1 m × 3 mm, 15% PPG on Diatomite; Column F, 3.5 m × 9 mm, 10% Carbowax 20 M on Chromosorb W; and Column G, 3.5 m × 9 mm, 20% 1.3-DCEP on Phasesep P (1,3-DCEP = 1,3-bis(cyanoethoxy)propane). Spectral data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 22759.

Preparation of 1,3-*Dienes*.—(a) *Homoallylic alcohols*. The ketone (0.2 mol) in dry ether was added slowly with stirring to allylmagnesium bromide [26] and the mixture was refluxed for 1 h. After cooling, it was poured onto ice–water, the precipitate was dissolved with dilute sulphuric acid, and the product was extracted with ether and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was fractionally distilled.

(b) *Dehydration*. The method is a modification of that of Lomas.[9] Distilled thionyl chloride (3.5 mmol) was added dropwise to the alcohol (2.5 mmol) in AnalaR pyridine (1 ml). The reaction mixture was stirred at 0 °C for 3 h, during which time the colour changed from yellow through orange to red, and then extracted twice with ether. The extracts were washed thoroughly with water to remove pyridine and then dried (K_2CO_3), after which the ether was removed under reduced pressure. (NOTE: Products of these dehydrations should be stored in a freezer, since rapid polymerisation occurs at room temperature and with sunlight.)

(E)-4,5,5-*Trimethylhexa*-1,3-*diene* (2c).—Pinacolone (28.0 g) was treated with allylmagnesium bromide to give 2,2,3-trimethylhex-5-en-3-ol (3c) (34.2 g, 86%), b.p. 61 °C at 14 Torr, $\nu_{max.}$ 3 480 and 3 080 (w), and 2 950 and 1 640 cm^{-1}; τ 4.10 (m, 1 H), 4.90 (m, 1 H, J_{gem} 2.0, J_{cis} 11.0 Hz), 4.98 (m, 1 H, J_{gem} 2.0, J_{trans} 16.0 Hz), 7.80 (m, 2 H), 8.10 (br, s, 1 H, removed by D_2O), 8.93 (s, 3 H), and 9.05 (s, 9 H). Dehydration of (3c) (28.9 g) with $SOCl_2$ (20.5 ml) and pyridine (97 ml) gave alkenes (16.9 g, 67%). G.l.c. (column A, 80 °C) showed 2 components which were separated by preparative g.l.c. (column F, 64 °C) and shown to be 2-t-butylpenta-1,4-diene (36% of mixture), $\nu_{max.}$ 3 050, 2 950, 1 815, 1 630, 1 420, 1 390, and 900 cm^{-1}; τ 4.25 (m, 1 H), 5.20 (m, 4 H), 7.24 (d, 2 H, J 6.0 Hz), and 8.94 (s, 9 H); and (*E*)-4,5,5-trimethylhexa-1,3-diene (2c) * (64% of mixture), $\nu_{max.}$ 2 950, 1 798 (w), 1 643, 1 480, 1 380, and 910 cm^{-1}; $\lambda_{max.}$ 236 nm (ε 10^4).

(Z)-4,5,5-*Trimethylhexa*-1,3-*diene* (1c).*—(*E*)-4,5,5-Trimethylhexa-1,3-diene (2c, 0.94 g) and acetophenone (0.91 g) in distilled n-pentane (200 ml) were irradiated with a medium pressure Hg lamp for 1 h, after which time g.l.c. (column D, 120 °C) showed 41% of the *Z*-isomer to be present.

The solvent was removed under reduced pressure and the product purified by column chromatography on silica, the dienes being eluted with light petroleum (b.p. 30—40° C). Adequate separation of the two isomers (1c) and (2c) could not be achieved using any of the preparative columns available, so that all spectral data of the *Z*-isomer was accumulated from a *Z*–*E* mixture; $\lambda_{max.}$ 237 nm with shoulder at lower wavelength.

4,5-*Dimethylhexa*-1,3-*dienes*. 3-Methylbutan-2-one (25.0 g) was treated with allylmagnesium bromide to give 2,3-dimethylhex-5-en-3-ol * (3b) (35.3 g, 95%), b.p. 57 °C at 15 Torr. Dehydration of (3b) (35.3 g) with $SOCl_2$ (28.2 ml) in pyridine (114 ml) gave alkenes (14.4 g, 50%). G.l.c. (column D, 120 °C) showed five components which were separated by preparative g.l.c. (column G, 50 °C) into 2-isopropylpenta-1,4-diene *,[27] (21% of hydrocarbon), 4,5-dimethylhexa-1,4diene *,[27] (40% of hydrocarbon), (Z)-4,5-dimethylhexa-1,3-diene * (1b), (14% of hydrocarbon), (E)-4,5-dimethylhexa-1,3-diene * (2b) (25% of hydrocarbon), and 4-chloro-4,5-dimethylhex-1-ene * (minor amount).

4-*Cyclopropylpenta*-1,3-*dienes*. Cyclopropyl methyl ketone (10.0 g) was treated with allylmagnesium bromide to give 2-cyclopropylpent-4-en-2-ol * (3d) (14.4 g, 96%). Dehydration of (3d) (14.4 g) with $SOCl_2$ (11.5 ml) in pyridine (46 ml) gave alkenes (3.56 g, 29%). G.l.c. (column C, 140 °C) showed three components which were separated by preparative g.l.c. (column F, 120 °C) into 2-cyclopropylpenta-1,4-diene * (25% of hydrocarbon), a mixture of (*E*)- and (*Z*)-4-cyclopropylpenta-1,3-dienes * (1d and 2d) (75% of hydrocarbon), and 4-chloro-4-cyclopropylpent-1-ene * (small amount).

The mixture of (*E*)- and (*Z*)-1,3-dienes, although seen as one peak when using PPG as liquid phase, was resolved into two components using PPGA (column D, 65 °C), and was separated on a preparative scale using column G at 60 °C to afford (*E*)-4-cyclopropylpenta-1,3-diene * (2d) (37% of hydrocarbon) and (*Z*)-4-cyclopropylpenta-1,3-diene * (1d) (38% of hydrocarbon).

4-*Methylhepta*-1,3-*dienes*.—Pentan-2-one (6.5 g) was treated with allylmagnesium bromide to give 4-methylhept-6-en-4-ol (3a) (9.05 g, 94%). Dehydration of (9c) (9.05 g) with $SOCl_2$ (7.4 ml) in pyridine (20 ml) gave alkenes (4.11 g, 52%). G.l.c. (column B, 68 °C) showed six components, separated preparatively using column G at 40 °C. Of the first component, amounting to 5% of the hydrocarbon pro-

duct, insufficient was collected to obtain a positive identification. The second and third products (in order of elution) were collected together and tentatively identified as: (*Z*)- and (*E*)-4-methylhepta-1,4-dienes * by order of elution from the g.l.c. and their ^{1}H n.m.r. spectra; yield 40% of hydrocarbon. The three remaining components were positively identified as (*Z*)-4-methylhepta-1,3-diene * (1a) (22% of hydrocarbon), (*E*)-4-methylhepta-1,3-diene (2a) (33% of hydrocarbon), and 4-chloro-4-methylhept-1-ene *.

4-Phenylpenta-1,3-diene.—Acetophenone (7.0 g) was treated with allylmagnesium bromide to give 2-phenylpent-4-en-2-ol * (8.6 g, 92%), b.p. 115—120 °C at 20 mmHg. Reaction of (3e) (8.6 g) with $SOCl_2$ (5.5 ml) in pyridine (20 ml) for 45 min gave 4-chloro-4-phenylpent-1-ene * (6) (3.6 g, 38%), b.p. 115 °C at 20 mmHg. G.l.c. analysis (column A, 110 °C) showed three components, the percentages of which varied with column temperature, corresponding to the chloro-compound and its dehydrochlorination products. To obtain samples of these products the preparative g.l.c. was run at a column temperature of 160 °C (column F) and an injection-port temperature of 190 °C. This system gave two components, collected and identified as (a) a mixture of 2-phenylpenta-1,4-diene (1e) (57% of total) and (b) (*E*)-4-phenylpenta-1,3-diene * (2e) (43%). The first fraction was separated into its two components (column D, 70 °C) and gave 2-phenylpenta-1,4-diene * (45% of initial mixture)[28] and (*Z*)-4-phenylpenta-1,3-diene * (1e) (12% of initial mixture).

Identification of 1,3-*Dienes by* [1,5] H-*Shift.*—(i) *t-Butyldienes.* A sample of the conjugated diene obtained from the dehydration of the alcohol (3c), known to be a single isomer (g.l.c.), was pyrolysed in a sealed glass vessel under vacuum at 240 °C for 1 h. G.l.c. (column A, 80 °C) showed 2 components in the product, the original diene and another diene of much shorter retention time. Separation by preparative g.l.c. (column F, 80 °C) enabled the new component to be identified as: (*Z*)-2-t-butylpenta-1,3-diene (7c), τ 4.08 (br d, 1 H, *J* 11.8 and 1.3 Hz), 4.22 (2 × q, 1 H, *J* 11.8 and 6.4 Hz), 5.15 (1 H, *J* 1.5 Hz), 5.37 (d, 1 H, *J* 1.5 Hz), 8.30 (2 × d, 3 H, *J* 6.4 and 1.3 Hz), and 8.94 (s, 9 H). Treatment of (7c) with a trace of acid afforded the *E*-isomer. A 2-t-butylpenta-1,3-diene of unknown stereochemistry has been reported.[29]

(ii) *Isopropyldienes.* A sample (70 mg) of the conjugated diene of *shorter* retention time, obtained from the dehydration of the alcohol (3b), was pyrolysed at 240 °C for 2.0 h. G.l.c. (column D, 120 °C) showed three new components which were separated by preparative g.l.c. (column G, 50 °C) to afford (*Z*)-2,3-dimethylhexa-2,4-diene (8) τ 4.20 (br d, 1 H, H-4, J_{cis} 12.0 Hz), 4.67 (2 × q, 1 H, H-5, J_{cis} 12.0, $J_{\text{H-Me}}$ 7.0 Hz), 8.34 (br s, 6 H), 8.43 (s, 3 H), and 8.49 (2 × d, 3 H, $J_{\text{H-Me}}$ 7.0, J_{allyl} 1.5 Hz); (*Z*)-2,3-dimethylhexa-1,3-diene (9) τ 4.49 (br t, 1 H, H-4, *J* 7.0 Hz), 5.11 (d, 1 H, *J* 2.0 Hz), 522 (br s, 1 H), 7.95 (m, 2 H, CH_2 of Et), 8.13 (s, 3 H, 2-Me), 8.24 (s, 3 H, 3-Me; irradiation at 8.24 decouples H-4 of allylic coupling), and 8.99 (t, 3 H, *J* 7.0 Hz, Me of Et); and (*E*)-2,3-dimethylhexa-2,4-diene (10) τ 3.62 (d, 1 H, J_{trans} 16.0 Hz, H-4), 4.57 (2 × q, 1 H, J_{trans} 16.0 Hz, $J_{\text{H-Me}}$ 7.0 Hz, H-5), 8.26 (br s, 9 H, 3 × Me), and 8.28 (d, 3 H, *J* 7.0 Hz, C6-Me).

(iii) *Phenyldienes.* A sample of the 1,3-diene of longer retention time obtained by dehydrochlorination of (6) was pyrolysed at 240 °C for 1 h. This afforded a new component of much shorter retention time, which was separated by preparative g.l.c. (column D, 128 °C) and shown to be (*Z*)-2-*phenylpenta*-1,3-*diene* (7e), τ 2.68 (m, 5 H, phenyl), 3.68 (br d, 1 H, *J* 7.2 Hz), 4.10 (2 × q, 1 H, *J* 7.2 and 6.4 Hz), 4.64 (m, 1 H, J_{gem} 2, *J* 0.7 Hz), 4.82 (m, 1 H, J_{gem} 2 Hz), and 8.35 Hz (2 × d, 3 H, *J* 6.4 and 2.0 Hz). Treatment of (7e) with a trace of acid afforded the *E*-isomer.

We thank the S.R.C. for the award of a research studentship (to M. J. C.) and for funds for g.l.c. equipment.

[9/1435 *Received*, 10*th September*, 1979]

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