# TRIENE ELECTROCYCLIZATIONS

## SOME STRUCTURE REACTIVITY RELATIONS'

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Abstract—Two stereoselective routes for the synthesis of trienes having a central *cis* double bond have been devised. These were employed for the synthesis of (Z)-1-(cyclohexen-1-yl)-1,3-butadiene (1), (Z,E)-1-(cyclohexen-1-yl)-1,3-pentadiene (2), (Z,Z)-1-(cyclohexen-1-yl)-1,3-pentadiene (3), 1,2-divinylcyclohexene (4), (E,Z)-1-phenyl-1,3,5-hexatriene (5), (Z,Z)-1-phenyl-1,3,5-hexatriene (6) and (E,Z)-1-(p-chlorophenyl)-1,3,5-hexatriene (7). Rates of the thermal electrocyclization and activation parameters were measured for these in inert solvents. The results are tabulated below.

Compound	$k_1 \times 10^{5} (sec^{-1})$	Temp (°C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1	12.8	132	29	-6
2	12.5	132	29	- 1
3	2.6	173	34	- 5
4	3.86	125	25	- 15
5	16.0	145	28	- 8
6	3.0	195		—
7	15.0	145	25	-18(?)

The results and their implications for transition state geometry are considered.

During the last eight years since the conservation of orbital symmetry theory was published,<sup>2</sup> the consequences of the theory have provided a reliable guide to the stereochemistry or the "allowed" nature of numerous concerted processes. Despite the power of the theory, it is not overly helpful in delineating details of transition state geometry and other means for obtaining such information must be employed. The most useful of these is the study of the rate response to structural alteration in the substrate. For the triene electrocyclic reaction symmetry reduces the number of different positions to three. In the present paper the rate response, primarily to alkyl substituents, in all three positions will be assessed. of the trienes desired in this study rests in formation of the central *cis* double bond. Some of our early attempts<sup>3</sup> to use semi-hydrogenation of dienynes for this purpose prompted a careful examination of the selectivity of this reaction in conjugated systems.<sup>4</sup> This showed that bond and stereoselectivity were high for enynes, but bond selectivity was much reduced in 1,5-dien-3-yne systems. Scheme 1 was therefore designed to use this enyne selectivity in preparing *cis*-trienes. This process is generally useful for the synthesis of trienes substituted at C<sub>1</sub> and C<sub>2</sub> of the hexatriene moiety. The final E<sub>2</sub> elimination step gives both *cis* and *trans* isomers when R<sub>3</sub> ≠ H and these were separated by preparative GLC in most cases.

Synthesis. The crucial problem for the synthesis

When  $R_3 = H$  the final step leads to low yields of

~ ...

$$R_{1}-CH = CR_{g}-C \equiv CH \xrightarrow{1. \text{LiNH}_{g}} R_{1}CH = CR_{g}-C \equiv C-CH_{g}-CHR_{g}$$

$$H_{g} \downarrow \text{Lindlar}$$

SCHEME 1.

the elimination product, the t-butyl ether being the major by-product. The problem was conveniently circumvented by treating the tosylate with anhydrous trimethylamine in acetone, and subsequently carrying out a low temperature Hofmann elimination with sodamide in liquid ammonia. Scheme 1 or its alternative with the Hofmann elimination was used to prepare (Z)-1-(cyclohexen-1-yl)-1.3-butadiene (1), (Z,E)-1-(cyclohexen-1-yl)-1,3-pentadiene (2), (Z,Z)-1-(cyclohexen-1-yl)-1,3-pentadiene (3), (E,Z)-1-phenyl-1,3,5-hexatriene (5),  $(\mathbf{Z},\mathbf{Z})$ -1-phenyl-1,3,5-hexatriene (6), and (E.Z)-1-(pchlorophenyl)-1,3,5-hexatriene (7).



For substituents on C<sub>4</sub> and/or C<sub>5</sub> Scheme 1 will not suffice and most routes for double bond formation in conjugated systems tend to give predominantly trans isomers. To alleviate this difficulty we chose to put the central double bond in a ring small enough to restrict its configuration to the cis form. This particular solution is of restricted value since it permits only alkyl substitution at the central carbons. Our synthesis (Scheme 2) was based on the reductive bis-dehydroxylation reaction previously used by Kuhn and his students' for preparation of a variety of polyenes. While the final step proceeds in disappointingly low yield, the route is economical step-wise and leads to no stereochemical ambiguities. Recently a second synthetic scheme leading to similar trienes has been developed.<sup>6</sup>

Rate measurements. Kinetic measurements were made by an ampule technique using dilute solutions of substrate in hydrocarbon solvents. All compounds showed good first order rates through at least two half-lives. Considerable difficulty was experienced with the phenyl substituted trienes, since they showed an extraordinary sensitivity to radical polymerization. Good kinetics were obtained only by using carefully purified and degassed solvents and by complete exclusion of oxygen. Analysis in all cases except 1 was made by GLC. For compound 2 it was not possible to operate at temperature low enough to exclude all rearrangement during analysis. From retention times and rearrangement rates it can be estimated that isomerization on the column would not exceed 10% of the triene present in the sample. No correction has been introduced to compensate for this error. Compound 1 was not cleanly separable from its product on any column, and analysis was made by UV spectroscopy. Rates for all compounds except 6 were measured at three or more temperatures to permit calculation of activation parameters. Results are shown in Table 1.

Structural assignments. For the group 1, 2 and 3 we used 1 as the structural prototype and a major effort was expended to provide full support for the assigned structure of that compound. Both the typical three fingered peak in the UV, and the ratio of olefinic to allylic to aliphatic protons in the NMR spectra conform to expectations based on structure 1. The same product is obtained by semihydrogenation of 4-cyclohexenyl-1-buten-3-yne and elimination of tosylate from 4-cyclohexenylcis-3-buten-1-yl tosylate.<sup>4</sup> That the one double bond capable of stereochemical ambiguity has the cis configuration is shown by (a) the disubstituted double bond in 4-cyclohexenyl-3-buten-1-ol has  $J_{AB} = 11.4$  Hz, (b) 1 has no IR band near 965 cm<sup>-1</sup>, (c) iodine catalyzed isomerization converts 1 to an isomer with an IR band at 965 cm<sup>-1</sup> and an UV spectrum showing a strong hyperchromic effect on the central peak, and (d) cyclization occurs thermally at 112° whereas trienes with a central trans double bond do not cyclize thermally below 300°.7

Compounds 2 and 3 possess one new double bond capable of geometric isomerism. In each case a sample having 1,2-dideuterio substitution was prepared and the NMR spectrum of the olefinic region unravelled to give the olefinic proton coupling,  $J_{AB}$ , of the ABX<sub>3</sub> pattern for the CH=CHCH<sub>3</sub> grouping. For 2 this coupling is 16 Hz typical of a



Compound	(°C)	Rate $\times 10^{3}$ (sec <sup>-1</sup> )	$\Delta H^{\ddagger}$ (kcal/mole)	Δ <i>S</i> ‡ (eu)
1	117.0	3.03	28	-6
	122.0	4.88		
	128.7	10.1		
	132.0	12.8		
	135.0	17-1		-
2	112.0	2.40	28	- 1
	119.5	4.26		
	125.0	6-41		
	130-0	<b>8</b> ⋅66		
	132.5	12.5		
	137.0	20.6		
3	172.7	2.59	33	- 5
-	182.6	5·79		
	1 <b>90</b> ·2	11.4		
	191·0	11.9		
4	125.0	3.86	25	- 15
	137-0	8.9		
	140.0	10.3		
	150-0	30-0		
	153-5	32.7		
5	125.0	3.0	28	- 8
-	145.0	16.0		
	165-0	<b>78</b> ⋅0		
6	195-0	3.0		
7	125.0	4∙0	24	- 18
	145.0	15.0		
	165-0	62.0		

Table 1. Rates and activation parameters for cyclization of trienes 1-7

trans double bond, and for 3  $J_{AB}$  is approximately 11 Hz. As a double check 3 was prepared by semihydrogenation of 1-cyclohexenyl-cis-3penten-1-yne which showed  $J_{AB} = 11.0$  Hz. All spectral properties were in agreement with the assigned structures.

The structure for 4 is fully confirmed by its spectral properties. Its UV spectrum is typical of a conjugated triene and its NMR spectrum shows the simplicity expected of so symmetric a substance, including olefinic peaks typical of vinyl groups and equivalent numbers of allylic and aliphatic methylene groups. Similarly structures of 5 and 7 are reasonably derived from their spectral properties. The central double bond in the triene is assigned a cis configuration from the mode of synthesis and the ease of thermal electrocyclization. trans Geometry at the aromatic substituted double bond was assigned from the NMR coupling for the ArCH=CH-group in the 6-aryl-5-hexen-3-yn-1-ols and the assumption that further reaction leads to no stereomutation. The overall skeleton for 5 was confirmed by quantitative hydrogenation (3 equivalents) to give n-hexylbenzene.

We did not prepare 6 in pure form. In the preparation of 1-phenyl-1-buten-3-yne the elimination gives about 90% trans and 10% cis isomers. Separation of these two on a preparative scale was not convenient, and the mixture was carried through the chain elaboration to give a mixture of stereoisomeric 6-phenyl-5-hexen-3-yn-1-ols. These could be separated by fractional distillation to give pure trans isomer and a fraction enriched in the cis form. This latter fraction was carried through the synthesis to give a mixture containing about 65% 6 and 35% 5 (GLC analysis). The configurational assignment is based purely on NMR data for the envnol and the mode of synthesis. However support for the assignment is given by the fact that the initial thermal isomerization product from 5 or 6 is the same compound.

The thermal product from 1 was assigned the structure 8 because it has the UV spectrum of a



homoannular diene, has a ratio of eleven aliphatic to three olefinic protons in the NMR, and dehydrogenation gave naphthalene. No other diene derived from the decalin skeleton fits these data. Thermal products 9 and 10 derived from 2 and 3 respectively show UV spectra of the homoannular diene type and identical NMR spectra having three olefinic protons and a Me doublet. That these are not identical is indicated by their ready separation on GLC columns. Thus they must differ in the configuration at  $C_1$ . An attempt to ascertain the stereochemistry at C1 and C84 for 9 and 10 via conversion to the lactones 11, three of the four diastereomers of which have established configurations,<sup>\*</sup> failed when oxidative cleavage of the diene gave products having only a singlet Me resonance.

Structure of the thermal product from 4 has not been ascertained with certainty. The product has the UV spectrum of a homoannular diene and its NMR spectrum shows the presence of two olefinic protons. As might be expected for the predicted product 12, the NMR spectrum of the material obtained shows a sharp olefinic peak (width at half height 3.5 Hz) and three types of aliphatic methylene protons in the ratio 1:1:1. Reduction leads to a mixture of *cis*- and *trans*-decalins and a third product, probably  $\Delta^{9.10}$ -octalin. Since Hückel and Krauss<sup>9</sup> have obtained an impure sample of hexahydronaphthalene assigned the structure 12, whose  $\lambda_{max}$  was at 262 nm, and the NMR spectrum





differs from that of the more stable diene 13,\* we believe the thermal product has the structure 12. Study of this problem was complicated by the appearance of a second thermal product which was assigned the structure 14 based on its ultraviolet and NMR spectra. Formation of this s-trans diene which was shown kinetically to result from adventitious catalysis, was attributed to the presence of traces of iodine probably retained in the triene despite washing with bisulfite. If so, it would suggest that use of this synthetic scheme to prepare trienes with double bonds capable of geometric isomerization under iodine catalysis might present problems, though it would have no effect in the present case.



Structures of products derived from 5. 6 and 7 can be treated together, since 5 and 6 give the same product, and the product from 7 was essentially assigned a structure by analogy with the results from 5. Heating either 5 or 6 gives an initial thermal product assigned the structure 15. Its UV spectrum shows it to be a homoannular diene with no conjugation to the phenyl group. This product forms a Diels-Alder adduct with N-phenylmaleimide and can be dehydrogenated to give biphenyl. Further heating of 15 gives a second isomer with a UV spectrum indicative of conjugation between the phenyl and the homoannular diene chromophores (16). By analogy with these findings and based on UV spectra data, the thermal products from 7 were assigned structures 17 and 18.

\*NMR spectra of 13 and 14 were provided through the courtesy of a referee.



#### DISCUSSION

The conservation of orbital symmetry predicts that the new single bond formed between  $C_1$  and  $C_6$ of a *cis*-triene will combine the two *p*-orbital lobes on the same side of the triene plane, i.e. a disrotatory process. This prediction has been confirmed experimentally.<sup>310</sup> One consequence of this rotation which appears to be quite general whatever reasonable geometry may be proposed for the transition state is that the two groups which are cis to the triene chain at  $C_1$  and  $C_6$  are forced to assume a more crowded position in the transition state than in the ground state. The expected rate retardation when the size of such a substituent is increased is clearly evident from the present results. Thus a methyl group in the cis position decreases the rate by about 100-fold. Not surprisingly a phenyl group depresses the rate by a larger amount, although the evidence on this point found in the present work conflicts somewhat with the brief mention by Schiess, Seeger and Suter<sup>6</sup> that (E,Z)-1,2-distyrylcyclohexene reacts only about 20× slower than the (E,E) isomer. Dreiding models show that (E,Z)-1,2-distyrylcyclohexene is seriously hindered and probably cannot reach coplanarity. The UV data support this conclusion. By contrast 6 is much less hindered and again the UV spectral data confirm the suggestion. Much of the ground state strain in the distyrylcyclohexene will be relieved in the transition state, a factor which may well account for the considerable difference in relative rates.

The most unexpected result obtained here is the almost complete lack of rate response to *trans* substituents on the terminal carbons. With the exception of very large groups no serious increase in steric strain would be anticipated in going from the ground to the transition state. However the hyb-



ridizational alteration from sp<sup>2</sup> to sp<sup>3</sup> at each terminal carbon of the triene system should reduce any stabilizing interaction of the substituent with the olefinic system. For a methyl substituent one can estimate the stabilizing effect of a trans-Me as 2.6 kcal/mole since the difference in heats of formation of 1-pentene and trans-2-pentene is 2.6 kcal/mole.<sup>18</sup> The value is in agreement with our finding<sup>3</sup> that (Z,Z,Z)-2,4,6-octatriene rearranges to (E,Z,Z)-2.4,6-octatriene presumably via (Z,Z)-1,3,5-octatriene even though that latter substance is not identifiable in the mixture at any time. Similarly one can estimate the stabilizing value of a phenyl group at ca 3.0 kcal/mole from the difference in heats of hydrogenation of 1,2- and 1,4dihydronaphthalenes.<sup>19</sup> From heats of hydrogenation Wheland<sup>20</sup> has given the excess resonance added for the double bond of styrene as 2.0 kcal/mole.

The data above show that if the methyl or phenyl group were completely disconnected from the olefinic system at the transition state both groups should reduce the rate of the cyclization because of the ground state stabilization. Contrarily the experiments show that neither alkyl nor aryl groups influence the rate appreciably. An obvious conclusion would be that the transition state has a strong resemblance to the ground state, but for a concerted process whose transition state is some 30 kcal/mole higher than the ground state in energy this seems difficult to justify. Our calculations<sup>21</sup> suggest that at the terminal carbons of the triene system rehybridization and sigma bond formation is well advanced at the transition state, hence little p-orbital character remains to allow stabilization of the type provided by alkyl or aryl groups to olefins. Apparently the stabilization effected is close to that supplied in the ground state.

The influence of substituents on  $C_3$  or  $C_4$  might well be expected to be minimal. No change in hybridization occurs and little structural change is needed to reach the transition state. Our model<sup>21</sup> also suggests that double bond character between  $C_3$  and  $C_4$  is not seriously reduced at the transition state. For the single example studied results conform to expectations.

Most interest centers on the results of substitution at  $C_2$  and  $C_3$ . The notion that concerted electrocyclic reactions of proper stereochemistry involve "aromatic" transition states<sup>22</sup> evokes the idea of a special stabilization inherent in such states. This has often been interpreted to mean that such transition states need little further stabilization, and thus that substituent effects on rate will inherently be of small magnitude.<sup>23</sup> The results found in Table 2 should disillusion chemists of the feeling that small rate effects are inevitable for these reactions. More than a single mode of action can be involved at these positions. Aside from the sort of ground state interaction (resonance, electronic effects, etc) noted for the substituents at  $C_1$  or  $C_6$  above, substituents at C<sub>2</sub> and C<sub>5</sub> can have marked steric effects. Of the three planar conformations possible for cis-hexatriene 19c can be excluded because of the extreme steric interactions of the cis-hydrogens at  $C_1$  and  $C_6$ . A substituent (Y) larger than hydrogen causes steric interactions of serious magnitude in both 19a and 19b. For the special case of Y-methyl this was recognized by Pauling<sup>24</sup> and the theory of the "hindered-cis" double bond was important in the development of understanding of polyene chemistry.25 While we have been unable to unearth data which would permit estimation of the magnitude of the energy effect of the Me group, the general difficulty associated with direct formation of "hindered-cis" double bonds by trans  $\rightarrow$  cis isomerization<sup>26</sup> suggests that the free energy difference between a trans and a "hindered-cis" double bond exceeds 3 kcal/mole. In the transition state this steric strain is expected to be largely relieved and this alone should increase the rate by one or two orders of magnitude for groups as large as Me.



Though one might assume that the influence of substituents other than of steric origin would be similar to those at  $C_3$  or  $C_4$ , the transition state calculated<sup>21</sup> indicates that the disrotatory motion leaves the p-orbitals at  $C_2$  and  $C_3$  badly isolated and thus subject to serious need for stabilization. Hence groups capable of stabilizing a radical center would be expected to provide more than a normal rate enhancement. This raises the question of what is meant by a normal rate enhancement. To calibrate this we have carried out a kinetic study of the influence of groups at C<sub>2</sub> of an allylic moiety in the Cope and Claisen rearrangements.<sup>27</sup> These show that a Me group (Claisen) at  $C_2$  slows the rate by less than 10%, while a phenyl group (Cope) increases the rate by 100-fold.

The rate enhancement of 3-fold for 1 and 2 is in the expected direction but is rather surprisingly small. Models suggest that the cyclohexane ring need not distort seriously during the reaction, and we believe it has no major influence on the result. Using the thermochemical data of Benson,<sup>28</sup> a stabilization energy of *ca* 0.5 kcal/mole can be estimated for a methylene group on a carbon radical. This suggests that the stabilizing influence of the methylene group at C<sub>2</sub> in the transition state is very small and can probably be ignored. Hence one concludes from the present data that the steric effect is smaller than might otherwise have been supposed.

Given the analysis above as correct one can associate the main rate enhancement of the carboxyl derivatives at  $C_2$  and  $C_3$  to stabilization effects

Compound	Rel. rate	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S$ ‡ (eu)	Ref
cis-Hexatriene	1.0	29.0	-5	7
(E,Z,E)-2,4,6-			-	
octatriene	1.0	29.0	-7	10a
(Z,Z,E)-2,4,6-				
octatriene	0.01	32.0	- 5	10a
2,6-Dimethyl-1,3,5-				
heptatriene	0.03	32.0	- 14	11
1	3.0	<b>29</b> ·0	-6	
2	3.0	29.0	- 1	
3	0.02	33·0	-5	
4	1.3	25.0	-15	
5	1-2	28.0	- 8	
6	0.005			
7	1.2	25.0	- 18	
(E,Z,Z,E)-1,8-				
diphenyi-1,3,5,7-				
octatetraene	0.03	-	_	12
2-Carbethoxy-1,3,5-				
hexatriene	$ca \ 2 \times 10^3$			13
2,5-Dicarbethoxy-				
1,3,5-hexatriene	$ca \ 2 \times 10^6$	_	_	14, 15
(E,E)-12,-distyryl-				
cyclohexene	1.2	_	<u> </u>	6
2,5-Di(N,N-dimethyl-				
carboxamido)-1,3,5-				
hexatriene	$ca \ 3 \times 10^{3}$	—	—	15
C <sub>8</sub> H <sub>3</sub> COOEt C <sub>8</sub> H <sub>3</sub>	1·4×10³	20.0	- 17·5	16
Me Me Me Me Me	0.02	27-4	- 19.0	17

 
 Table 2. Relative rates for electrocyclization of some simple acyclic trienes using cis-nexatriene as a standard

rather than steric. Though we lack comparison data for the Cope or Claisen rearrangement, it is clear that substituents at these positions do indeed produce much larger rate alterations than at the other positions, in accord with expectations derived from our relatively naive model.<sup>21</sup>

#### EXPERIMENTAL

1-(Cyclohexen-1-yl)-1-butyn-4-ol. This compound was prepared from ethynylcyclohexene<sup>29</sup> and ethylene oxide in 80% yield according to the procedure of Marvell and Tashiro.<sup>4</sup>

(Z)-1-(Cyclohexen-1-yl)-1-buten-4-ol. A sample, 5.06 g (0.034 mole), of 1-(cyclohexen-1-yl)-1-butyn-4-ol was hydrogenated over 0.35 g of Lindlar<sup>30</sup> catalyst in 50 ml light petroleum containing a few drops of synthetic quinoline. The product was isolated by distillation, b.p. 63-65° (0-1 mm);  $n_{D}^{50}$  1.5194; IR (neat) 3285, 1632, 1045 cm<sup>-1</sup>; NMR (CCL)  $\delta$  5·0–5·9 (m, 3H), 4·76 (OH), 3·52 (t, 2H), 2·50 (t, 2H), 2·08 (m, 4H), 1·58 (m, 4H); yield 81%. (Found: C, 79·11; H, 10·33. Calc. for C<sub>10</sub>H<sub>16</sub>O: C, 78·90; H, 10·59%).

(Z)-1-(Cyclohexen-1-yl)-1,3-butadiene (1). To a soln of 24 g (0.13 mole) p-toluenesulfonyl chloride in 12 ml pyridine which had been cooled in an ice bath was added 16.6 g (0.11 mole) (Z)-1-(cyclohexen-1-yl)-1-buten-4-ol. The mixture was stirred under N<sub>2</sub> for 24 h, and after addition of cold water, the product was taken up in ether. The ether soln was washed with water, dil phosphoric acid, NaHCO<sub>3</sub> aq and again with water. The ether soln was dried (K<sub>2</sub>CO<sub>3</sub>) and a crude tosylate (98%) was isolated by evaporation of the ether. The crude tosylate was used directly in the next step.

A soln containing 22.5 g (0.074 mole) of the above tosylate in 10 ml DMSO was cooled in an ice bath under N<sub>2</sub>. To this was added dropwise a soln containing 6.6 g (0.065 mole) t-BuOK in 40 ml DMSO. After addition was complete, the soln was stirred 15 min and reaction was quenched by addition of a large excess water. The mixture was extracted with pentane and the pentane soln was washed with water and then dried ( $K_2CO_3$ ). The product was isolated by distillation, b.p. 59–61° (3.5 mm);  $n_2^{20}$  1.5474; 4.95 g (50%); IR (neat) 3030, 1625, 900 cm<sup>-1</sup>; UV max (EtOH) 259 (18,600), 264 (20,800), 272 (17,300); NMR (CCl<sub>4</sub>)  $\delta$  6.6–7.2 (m), 4.9–5.9 (m), 2.13 (m), 1.58 (m). (Found: C, 89-74; H, 10-51. Calc. for C<sub>10</sub>H<sub>14</sub>: C, 89-52; H, 10-48%).

1-(Cyclohexen-1-yl)-1-pentyn-4-ol. This alcohol was prepared on a 0-7 mole scale from ethynylcyclohexene and propylene oxide according to the procedure described for 1-(cyclohexen-1-butyn-4-ol. The product had the following properties, b.p. 71-72° (0.08 mm);  $n_{0}^{\infty}$  1.5180; IR (neat) 3400, 1115 cm<sup>-1</sup>; UV max 225 (13,100); NMR (CCl<sub>3</sub>)  $\delta$  5.96 (1H), 4.2 (s, OH), 3.87 (sextet, 1H, J = 7), 2.40 (d, 2H, J = 7 Hz), 2.07 (m, 4H), 1.57 (m, 4H), 1.23 (d, 3H, J = 7 Hz). (Found: C, 80.19; H, 9.95. Calc. for C<sub>11</sub>H<sub>16</sub>O: C, 80.45; H, 9.81%).

(Z)-1-(Cyclohexen-1-yl)-1-penten-4-ol. A sample of 1-(cyclohexen-1-yl)-1-pentyn-4-ol was reduced with Lindlar catalyst as described for the preparation of (Z)-1-(cyclohexen-1-yl)-1-buten-4-ol. The product was isolated by distillation, b.p. 70-71° (0·2 mm);  $n_{20}^{\infty}$  1·5101; UV max 228 (12,200); NMR (CCl<sub>4</sub>)  $\delta$  5·08-5·92 (series of peaks, 3H), 4·34 (s, OH), 3·77 (sextet, 1H, J = 7 Hz), 2·45 (m, 2H), complex centered at 1·6, 1·17 (d, 3H, J = 7 Hz). (Found: C, 79·27; H, 10·70. Calc. for C<sub>11</sub>H<sub>18</sub>O: C, 79·46; H, 10·91%).

1-(Cyclohexen-1-yl)-1,3-pentadienes. A crude tosylate prepared in 98% yield from (Z)-1was (cyclohexen-1-yl)-1-penten-4-ol according to the procedure described for (Z)-1-(cyclohexen-1-yl)-1-buten-4-yl tosylate. A soln containing 13.7 g (0.043 mole) in 5 ml DMSO was treated with 3.27 g (0.032 mole) t-BuOK in 20 ml DMSO as described for the preparation of 1. The product was isolated as before, b.p.  $65-68^{\circ}$  (2 mm);  $n_{D}^{20}$ 1.5430; 2.3 g (48%). GLC analysis on a 14 ft × in 20% Carbowax 20 M column at 130° showed that both (Z,E) and (Z,Z) isomers were formed in a ratio of 72:28.

(Z,E)-1-(Cyclohexen-1-yl)-1,3-pentadiene (2). The mixture of isomers obtained above was separated by preparative GLC on a 15 ft  $\times_{3}^{3}$  in 20% Carbowax 20 M column, IR 3020, 980, 725 cm<sup>-1</sup>; UV max 250 (16,700), 269 (22,200), 287 (18,700); NMR (CCL)  $\delta$  1.70 (complex mult), 2.15 (m), 5-2-6-8 (series of peaks). (Found: C, 89-00; H, 10-83. Calc for C<sub>11</sub>H<sub>16</sub>: C, 89-12; H, 10-88%).

A sample of (Z,E)-1-(cyclohexen-1-yl)-1,2dideuterio-1,3-pentadiene obtained by semihydrogenation of 1-(cyclohexen-1-yl)-1-pentyn-4-ol with deuterium showed an NMR spectrum having the AB portion of an ABX<sub>3</sub> system in the olefinic region, 5.57 (two quartets, 1H,  $J_{AB} = 17$ ,  $J_{AX} = 7$  Hz), 6.64 (d with additional splitting, 1H,  $J_{AB} = 17$ ,  $J_{BX} = 1.5$  Hz).

(Z,Z)-1-(Cyclohexen-1-yl)-1,3-pentadiene (3). A sample of 3 was obtained from the mixture of 2 and 3 by GLC separation as above. The GLC purified 3 had the following properties, UV max 270 (17,100); NMR (CCl.)  $\delta$  1.62 (m), 1.73 (d, J = 7 Hz), 2.17 (m), 5.0–7.0 (complex series of peaks). (Found: C, 89.08; H, 10.84. Calc. for C<sub>11</sub>H<sub>18</sub>: C, 89.12; H, 10.88%).

From the deuteration described above a small amount of (Z,Z)-1-(cyclohexen-1-yl)-1.2-dideuterio-1.3-pentadiene was isolated by GLC. It was possible only to show that the downfield olefinic proton of the ABX, system appeared at 6.6 ppm and had  $J_{AB} \sim 11$  Hz.

A sample of (Z)-1-(cyclohexen-1-yl)-3-penten-1-yne

(see below) was semihydrogenated over Lindlar catalyst under conditions described above. From the mixture of products a sample of 3 was obtained by preparative GLC on the 15 ft  $\times_{\frac{3}{2}}^{\frac{3}{2}}$  in 20% Carbowax 20 M column. The spectral properties of this sample were the same as those noted above.

1-(Cyclohexen-1-yl)-3-penten-1-ynes. A tosylate was prepared from 1-(cyclohexen-1-yl)-1-pentyn-4-ol as described in the preparation of 1. The tosylate was treated with t-BuOK as described in the preparation of 1. After work-up the mixture of isomeric enynes was subjected to preparative GLC on the 15 ft  $\times$  in 20% Carbowax 20 M column. (E)-1-(Cyclohexen-1-yl)-3-penten-1-yne eluted first, NMR (CCl<sub>4</sub>)  $\delta$  1-60 (m), 1-74 (d,  $J = 6 \cdot 0$  Hz), 2·10 (m), 5·51 (broadened d,  $J_{AB} = 17$  Hz), 5·99 (two overlapping quartets,  $J_{AB} = 17$ ,  $J_{Ax} = 6 \cdot 0$  Hz), 5·97 (s); and constituted 76% of the mixture. This product was not studied further.

(Z)-1-(Cyclohexen-1-yl)-3-penten-1-yne was also isolated by GLC, NMR (CCl<sub>4</sub>)  $\delta$  1.67 (m), 1.83 (d, J = 6.6 Hz), 2.11 (m), 5.52 (broad doublet,  $J_{AB} = 11$  Hz), 5.84 (overlapping quartets,  $J_{AX} = 6.6$  Hz), 5.95 (broad s); IR (CCl<sub>4</sub>) 710 cm<sup>-1</sup>. (Found: C, 89.75; H, 9.95. Calc. for C<sub>11</sub>H<sub>14</sub>: C, 90.35; H, 9.65%).

1-Phenyl-3-butyn-1-ol. To a soln containing 0.22 mole sodium acetylide in 300 ml liquid ammonia was added 12.8 g (0.11 mole) styrene oxide in 50 ml anhyd ether. After the mixture had been stirred for 24 hr, the ammonia was allowed to evaporate and 100 ml ether was added to the residue. The mixture was treated with ammonium chloride, and the ether layer was washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Distillation gave 11.2 g (73%), b.p. 72-75° (0.25 mm);  $n_{D}^{27}$  1.5430, IR (neat) 3420, 3250, 3050, 2120, 750 and 690 cm<sup>-1</sup>; NMR (CCL)  $\delta$  1.85 (t, 1H, J = 3 Hz), 2.40 (d of d, 2H, J = 7, J = 3 Hz), 4.57 (t, 1H, J = 7 Hz), 7.15 (s, 5H). Lit<sup>32</sup> b.p. 85° (0.5 mm);  $n_{D}^{20}$  1.5472.

1-Phenyl-1-chloro-3-butyne. The above alcohol (7.5 g, 0.05 mole) was added dropwise to 11.7 g (0.056 mole) PCl<sub>3</sub>. The mixture was stirred vigorously while being slowly warmed to 90°. The clear yellow soln was cooled to 0° and excess ice was added cautiously. The organic products were taken up in ether, and the ether soln was washed with water and then dil NaHCO<sub>3</sub> aq and dried (K<sub>2</sub>CO<sub>3</sub>). Distillation gave 8.0 g (94%) of liquid, b.p. 37-39° (0.05 mm);  $n_{D}^{22}$  1.5480 [lit<sup>32</sup> b.p. 70° (3 mm);  $n_{D}^{20}$  1.5550]; IR (neat) 3300, 2120, 750 and 695 cm<sup>-1</sup>; NMR (CCL<sub>4</sub>) & 1.9 (t, 1H, J = 3 Hz), 2.85 (d of d, 2H, J = 7, J = 3 Hz), 4.82 (t, 1H, J = 7 Hz), 7.2 (s, 5H).

1-Phenyl-1-buten-3-yne. The above chloride (11.6 g, 0.07 mole) was added dropwise to 150 ml of 1.0 N sodium isopropoxide soln in isopropyl alcohol. After the soln had been heated 5 h at reflux, it was cooled to 0° and 75 ml pentane was added followed by sufficient water to cause separation of layers. The pentane layer was isolated and dried (K<sub>2</sub>CO<sub>3</sub>). The product, 5.4 g (60%), was isolated by distillation, b.p. 35-37° (0.25 mm); n<sub>D</sub><sup>26</sup> 1.6030, UV max (EtOH) 282 (30,000) [lit.<sup>14</sup> b.p. 56-60° (5 mm); n<sup>21</sup><sub>D</sub> 1 6068; UV max 288 (20,000)]; IR 3300, 2120, 950, 725 and 695 cm<sup>-1</sup>. GLC analysis on a 10 ft ×<sup>1</sup><sub>8</sub> in 4% Ucon polar on Chromosorb G at 145° showed two products in a 9:1 ratio. The dominant (E) isomer had an NMR spectrum (CCl<sub>4</sub>)  $\delta$ 2.91 (d, 1H, J = 3 Hz), 6.00 (d of d, 1H, J = 18, J = 3 Hz), 6.90 (d, 1H, J = 18 Hz), 7.2 (s, 5H). The minor product, (Z) isomer, had NMR (CCL)  $\delta$  3.25 (d, 1H, J = 3 Hz), 5.60 (d of d, 1H, J = 12, J = 3 Hz), 6.65 (d, 1H, J = 12 Hz), 7.2 (s, 5H).

The isomers were not separated at this point but the mixture was used directly for further synthesis.

6-Phenyl-5-hexen-3-yn-1-ol. The Grignard reagent of 1phenyl-1-buten-3-yne was prepared by heating under reflux in a  $N_2$  atmosphere a soln containing 12.8 g (0.10 mole) of the envne and 0.14 mole ethyl Grignard reagent in 250 ml ether until ethane evolution ceased. The acetylenic Grignard separated as a dark oil when the soln was cooled to  $0^{\circ}$ . A soln containing 6.6 g (0.15 mole) ethylene oxide in 10 ml ether was added and the mixture was stirred under N<sub>2</sub> for 6 h at 5-10°. Dil H<sub>2</sub>SO<sub>4</sub> (25 ml) was added and the ether layer was separated, washed with NaHCO<sub>3</sub> aq and dried (K<sub>2</sub>CO<sub>3</sub>). Distillation gave a colorless liquid, 11.3 g (66%), b.p. 98-101° (0.005 mm); UV max (EtOH) 284 nm (30,000); IR 3600, 2210, 1050, 950, 725 and 695 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  2.6 (t of d, 2H, J=3, J=6 Hz), 3.7 (t, 2H, J = 6 Hz), 5.9 (d of t, 1H, J = 16, J = 3 Hz), 6.8(d, 1H, J = 16 Hz), 7·1 (s, 5H). (Found: C, 83·80; H, 7·20. Calc. for C<sub>12</sub>H<sub>12</sub>O: C, 83.69; H, 7.02%).

GLC analysis on an SE-30 column at 130° gave 8.5% (Z) isomer (eluted first) and 91.5% (E) isomer. Simple fractional distillation through a short Vigreux column gave a partial separation with pure (E) isomer in the latter fractions.

(Z,E)-6-Phenyl-3,5-hexadien-1-ol. The above enynol (11·3 g, 0·064 mole) was hydrogenated in 35 ml EtOAc, containing 10 mg synthetic quinoline, over 200 mg Lindlar catalyst. The catalyst was removed by filtration and the product was isolated by distillation, b.p. 99-100° (0·005 mm); UV max (EtOH) 280 nm (23,000); IR 3400, 3050, 1050, 960, 730 and 695 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  2·4 (q, 2H, J = 7 Hz), 3·5 (t, 2H, J = 7 Hz), 5·5-6·9 (series of peaks, 4H), 7·3 (broad s, 5H). (Found: C, 82·58; H, 7·93. Calc. for C<sub>12</sub>H<sub>14</sub>O: C, 82·72; H, 8·10%).

(Z,E)-N-(6,Phenyl-3,5-hexadien-1-yl)-N,N,N-trimethylammonium p-toluenesulfonate. To a cold (0°) slurry of 5.4g (0.028 mole) p-toluenesulfonyl chloride and 4.5 ml  $\gamma$ -collidine was added 4.5g (0.026 mole) of the above dienol in 4.5 ml collidine. The mixture was stirred 30 h at 0° under N<sub>2</sub>. Water was added and the organic material was taken up in ether. The ether soln was washed with dil phosphoric acid, dil NAHCO, aq and water. The soln was dried (K<sub>2</sub>CO<sub>3</sub>) and the crude tosylate, 7.7g (90%), was isolated by removal of the ether.

A soln of the above tosylate in ca 6 ml anhyd acetone was placed in two Pyrex tubes. The soln was degassed under N<sub>2</sub> and with careful exclusion of moisture, and the tubes were finally cooled in a Dry-Ice bath. An equal volume of anhyd trimethylamine was added to each tube which was then sealed. The quaternary salt forms in quantitative yield in 6 h at room temp. The hygroscopic solid was isolated by filtration, m.p. 200-205°; UV max (90% EtOH) 280 nm (16,000). (Found: C, 68-08; H, 7-44. Calc. for C<sub>22</sub>H<sub>29</sub>NSO<sub>3</sub>: C, 68-20; H, 7-54%).

(E,Z)-1-Phenyl-1,3,5-hexatriene (5). All steps in the following procedure must be carried out under oxygen-free N<sub>2</sub>. To a suspension of potassium amide (0.018 mole) in 700 ml liquid ammonia was added a slurry of 2.3 g (0.006 mole) quaternary salt in 5 ml dry pentane. The soln was stirred for 3 hr and 6.0 g ammonium chloride was added. The ammonia was allowed to evaporate, and pentane was added during evaporation to keep the soln volume at about 200 ml. The ppt was removed by filtration under N<sub>2</sub> and the solvent was removed *in vacuo*. The product was a low melting white solid, 600 mg (64%); UV max (cyclohexane) 308 nm (53,000); IR (CCl<sub>4</sub>) 3100, 1625, 960, 725 and 695 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  5.0–7.1 (series of peaks), 7.20 (m, 5H). Upon exposure to air the product decomposes to a gummy material. (Found: C, 92-13; H, 7.56. Calc. for C<sub>12</sub>H<sub>12</sub>: C, 92.26; H, 7.74%).

Hydrogenation of 100 mg of the above triene over Pt<sub>2</sub>O oxide in pentane gave 70 mg (68%) of a colorless liquid,  $n_D^{23}$  1.4835 whose spectral and GLC properties matched those of an authentic sample of *n*-hexylbenzene.

(Z,Z)-1-Phenyl-1,3,5-hexatriene (6). A sample of 6phenyl-5-hexen-3-yn-1-ol enriched in the *cis* isomer was carried through the procedure described above for preparation of 5, to give a sample of 1-phenyl-1,3,5-hexatriene containing 60% of 6 and 40% of 5 via GLC analysis on a 10 ft × $\frac{1}{2}$  in 4% Ucon polar on Chromasorb G ACDWS at 125°, UV (max) 306-308 nm. No attempt was made to purify the material further.

β-Chlorostyrene oxide. A soln of 187 g (1·3 moles) of β-chlorostyrene<sup>34</sup> in 2100 ml methylene chloride was cooled to 0° and 2·0 moles peracetic acid in AcOH containing 20 g AcONa was added over a 1 h period. The mixture was stirred for 30 h at 10–12° and then 1500 ml of water was added. The mixture was worked up as usual<sup>35</sup> to give 125 g (60%) of a colorless liquid, b.p. 54–56° (0·3 mm);  $n_{2}^{20}$  1·5510 [lit.<sup>36</sup> b.p. 82–86 (4 mm),  $n_{2}^{20}$  1·5541].

1-(p-Chlorophenyl)-3-butyn-1-ol. This was prepared on 0·5 molar scale from p-chlorostyrene oxide exactly as described for preparation of 1-phenyl-3-butyn-1-ol. The colorless liquid was obtained in 65% yield, b.p. 78-80° (0·2 mm); m.p. 30-32°; IR 3590, 3300, 2120, 1060 and 830 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  1·90 (t, 1H, J = 3 Hz), 2·55 (d of d, 2H, J = 6, J = 3 Hz), 4·60 (t, 1H, J = 6 Hz), 7·15 (s, 4H). (Found: C, 66·33; H, 5·10. Calc. for C<sub>10</sub>H<sub>9</sub>ClO: C, 66·48; H, 5·01%).

1-(p-Chlorophenyl)-1-buten-3-yne. The above alcohol (11 g, 0.061 mole) was dissolved in 10 ml anhyd pyridine and the soln was cooled to 10°. To this was added a soln containing 22.8 g (0.15 mole) POCl, in 20 ml pyridine, and the mixture was heated at 50° until a clear soln resulted. The soln was mixed with ice and the organic products were taken up in ether. The ether extracts were washed with dil phosphoric acid, dil NaHCO<sub>3</sub> and water, and then the soln was dried (MgSO<sub>4</sub>). The crude chloride 9.5 g (77%) was used directly in the next step.

Chloride (8 g) was treated with sodium iso-propoxide as described for preparation of 1-phenyl-1-buten-3-yne. The product was purified by sublimation, m.p.  $51-53^{\circ}$ ; UV max (EtOH) 283 nm (39,000); IR 3250, 2120, 950 and 855 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  3.00 (d, 1H, J = 3 Hz), 5.85 (d of d, 1H, J = 17, J = 3 Hz), 6.80 (d, 1H, J = 17 Hz), 7.10 (s, 4H). The presence of *ca* 10% of the *cis* isomer was indicated by 5.57 (d of d, 1H, J = 12, J = 3 Hz), 6.60 (d, 1H, J = 12 Hz). (Found: C, 73.68; H, 4.29. Calc. for C<sub>10</sub>H<sub>7</sub>Cl: C, 73.86; H, 4.34%).

(E)-6-(p-Chlorophenyl)-5-hexen-3-yn-1-ol. This substance was prepared from the enyne above by the procedure described under 6-phenyl-5-hexen-3-yn-1-ol. It was purified by sublimation, m.p. 93–95°; UV max 285 nm (30,000); IR 3590, 3050, 1050 and 810 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  2·70 (t of d, 2H, J = 6, J = 3 Hz), 3·80 (t, 2H, J = 6 Hz), 6·10 (d of t, 1H, J = 17, J = 3 Hz), 6·80 (d, 1H, J = 17 Hz), 7·20 (s, 4H). (Found: C, 69·93; H, 5·39. Calc. for C<sub>12</sub>H<sub>11</sub>ClO: C, 69·74; H, 5·37%).

(E,Z)-6-(p-Chlorophenyl-3,5-hexadien-1-ol. The above alcohol was reduced as described for 6-phenyl-3,5hexadien-1-ol. A once sublimed product, m.p. 94–96°; IR 3050, 940, 860 and 810 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  2·60 (q, 2H, J = 7 Hz), 3·60 (t, 2H, J = 7 Hz), 5·2–7·1 (complex, 4H), 7·2 (s, 4H), was obtained in 80% yield. (Found: C, 69·01; H, 6·25. Calc. for C<sub>12</sub>H<sub>13</sub>ClO: C, 69·06; H, 6·28%).

(E,Z)-N-[6-(p-Chlorophenyl) -3,5- hexadien -1- yl]-

N,N,N- trimethylammonium p-toluenesulfonate. This salt was prepared from the above dienol via the tosylate as described for the non-chlorinated derivative above. The salt, m.p.  $181-188^{\circ}$  (d) was obtained in near quantitative yield. (Found: C, 62.48; H, 6.76. Calc. for C<sub>22</sub>H<sub>28</sub>ClNO<sub>3</sub>S: C, 62.62; H, 6.69%).

(E,Z)-1- $(\beta$ -Chlorophenyl)-1,3,5-hexatriene (7). This triene was prepared from the above quaternary salt as described for 5. The product was a white solid, m.p. 25-28°, UV max 217 (53,000); NMR (CCl<sub>4</sub>)  $\delta$  5·1-6·9 (complex series of peaks), 7·25 (d, 4H). The solid decomposes to form a yellow pentane insoluble material when exposed to air. No satisfactory analysis was obtainable.

2-Hydroxy-2-vinylcyclohexanone. A soln of 33.6 g(0.30 mole) 1,2-cyclohexanedione in 100 ml THF was added dropwise to a soln containing vinyl-magnesium bromide prepared from 18.8 g (0.77 g-atom) Mg and 55.0 g(0.52 mole) vinyl bromide in 80 ml THF. The reaction soln was stirred for 12 h and 100 ml sat ammonium chloride soln was added. The aqueous layer was extracted with ether and the ether soln was dried (MgSO<sub>4</sub>). The solvent was removed to give a liquid, b.p.  $40-45^{\circ}$  (0.03 mm); IR 3500, 3095,  $1710 \text{ cm}^{-1}$  [it.<sup>37</sup> IR 3500, 3090, 1710]; NMR (CCl<sub>4</sub>)  $\delta$  1.76 (m, 4H), 2.14 (m, 2H), 2.50 (m, 2H), 3.81 (s, OH), 5.30 (m, 2H), 6.12 (m, 1H).

1,2-Divinyl-1,2-cyclohexanediol. To a cold (0°) soln containing 0·33 mole vinylmagnesium bromide in 100 ml THF was added 23 g (0·16 mole) of the above ketone in 100 ml THF. The reaction was allowed to proceed 12 h and the product was worked up as described under 2-hydroxy-2-vinylcyclohexanone. Distillation gave 5 g (18%) colorless viscous liquid, IR 3600, 3100, 1640 [lit.<sup>37</sup> 3612, 3090, 1630]; NMR (CCl.)  $\delta$  1·56 (m, 8H), 2·40 (m, 2H), 5·4 (series of peaks, 4H), 6·1 (series of peaks, 2H).\*

1,2-Divinylcyclohexene (4). The present method is adapted from the procedure of Kuhn and Winterstein<sup>38</sup> for oxidative removal of two OH groups. A soln containing 34.0 g (0.06 mole) diphosphorus tetraiodide<sup>39</sup> in 350 ml CS<sub>2</sub> was prepared using a Soxhlet extractor. To this was added dropwise a soln containing 5.0 g (0.03 mole) of the above diol in 60 ml anhyd pyridine. The mixture turned dark brown almost immediately, and the soln was stirred overnight. The CS<sub>2</sub> was removed in vacuo and the residual material was extracted thoroughly with ether. The ether extracts were washed with 2 N NaOH, 12% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln and finally with sat Na<sub>2</sub>SO<sub>4</sub> aq. The ether soln was dried (MgSO<sub>4</sub>) and the ether was removed giving 4.0 gcrude product. Chromatography over 10 g silica gel using hexane as eluant gave 1.2 g triene which analyzed by GLC (5% Carbowax 20 M column at 120°) as 75% pure triene, yield 22%. The yields are variable ranging from 10-25%. A GLC purified sample showed the following properties, UV max (EtOH) 260 (25,000), 269 (30,100), 279 (20,800); IR (CCL) 1.66 (broad m, 4H), 2.25 (broad m, 4H), 5.1 (series of peaks, 4H), 6.9 (series of peaks, 2H). (Found: C, 89.36; H, 10.70. Calc for C<sub>10</sub>H<sub>14</sub>: C, 89.49; H, 10.51%).

Thermal reactions. All trienes were heated in dilute soln in hydrocarbon solvents in sealed tubes. Pyrex bomb tubes were prepared by washing with dil NH<sub>4</sub>OH, distilled water, acetone and ether. After drying they were heated under N<sub>2</sub> to a red heat and then cooled slowly to room temp. Samples were carefully degassed, sealed under  $N_2$  and heated in a thermostatted bath.

Rate studies. All rate studies were carried out using dilute solns of trienes in hydrocarbon solvents in sealed tubes. Pyrex tubes were prepared as described for thermal reactions, solns were degassed and the tubes were sealed under N<sub>2</sub>. A series of these ampoules were heated in a thermostatted bath  $(\pm 0.1^\circ)$  and these were removed one at a time at selected intervals and quenched in a Dry-Ice bath. In all cases except 1 analysis was made by GLC using the conditions noted below.

Compounds 2 and 3 on 14 ft  $\times \frac{1}{8}$  in 20% Carbowax 20 M on firebrick at 120°.

Compound 4 on  $10 \text{ ft} \times \frac{1}{6} \text{ in } 4\%$  Ucon-polar on Chromasorb G AW DMCS at 65°.

Compounds 5, 6, and 7 on the same column as 4 but at  $130^{\circ}$ .

Analysis for compound 1 was carried out using a Cary 15 UV spectrometer at 265 nm. All reactions followed good first order rates to at least two half-lives, and the data are shown in Table 1.

1,2,3,4,8,8a-Hexahydronaphthalene (8). A soln of 1·11 g of 1 in 50 ml purified heptane was heated in a sealed tube at 145° for 6 h. The product was isolated by distillation in an alembic, b.p. 62-65° (7 mm), UV max 267 nm (3400), NMR (CCl<sub>4</sub>)  $\delta$  1·6 (broad m), 2·1 (broad m), 6·1 (broad s) with the area ratio of approximately 1:1·7:2·1. (Found: C, 89·85; H, 10·43. Calc. for C<sub>10</sub>H<sub>4</sub>: C, 89·52; H, 10·48%).

A sample of 8, 1.3 g (0.01 mole), was heated under a  $N_2$  stream for 20 h at 225° with 0.1 g of 10% Pd-C. The product which sublimed from the mixture was dissolved in EtOH and treated with picric acid. A picrate, m.p. 150° [lit.<sup>40</sup> m.p. 149°], was obtained.

8-Methyl-1,2,3,4,8,8a-hexahydronaphthalenes (9 and 10). A sample of trienes 2 and 3 obtained directly from the synthesis described above without separation of isomers was heated at 200° for 2 h. The products were identified by the amounts produced, and they were separated by GLC on a 15 ft  $\times \frac{3}{4}$  in 20% Carbowax 20 M column at 150°. The product 9 from 2 elutes later than that from 3. Compound 9 has the following properties, UV max 270 (4500), NMR (CCL)  $\delta$  0.98 (d, 3H, J = 6.7 Hz), 1·1-2·0 (broad m, ca 6H), 2·0-2·5 (broad s, ca 4H), 5·4-5·8 (broad m, ca 3H). (Found: C, 88·76; H, 10·82. Calc. for C<sub>11</sub>H<sub>16</sub>: C, 89·12; H, 10·82%).

The product 10 elutes first and has spectral properties identical to those given for 9. (Found: C, 88-90; H, 10-97. Calc. for  $C_{11}H_{16}$ : C, 89-12; H, 10-82%).

Thermal product from 4 (12). A soln of 4 in cyclohexane was heated in a sealed tube for 18 h at 125°. The product was collected from GLC on a 5% Carbowax 20 M column at 120°, UV max (EtOH) 263 nm (4830) [lit.<sup>9</sup> 262 nm]; NMR (CCL)  $\delta$  1.54 (m, 4H), 1.95 (m, 4H), 2.23 (m, 4H), 5.39 (m, 2H); mass spectrum m/e (rel. intensity) 134 (67), 119 (43), 106 (22), 91 (100).

Hydrogenation of the above material over  $PtO_2$  gave a mixture containing *cis* and *trans*-decalin (GLC comparison with authentic material).

1,2,3,5,6,7-Hexahydronaphthalene (14). A sample of 4 in cyclohexane was heated in a sealed tube for 24 h at 150°. The produce was collected from GLC separation on a 5% Carbowax 20 M column at 120° giving a colorless liquid, UV max (EtOH) 242 nm (17,400) [lit.° 237 (14,600)]; NMR (CCl.)  $\delta$ , 1.66 (m, 4H), 2.13 (m, 8H), 5.31 (broad s, 2H) [matches spectrum furnished<sup>10</sup>]; mass spectrum m/e (rel. intensity) 134 (48), 119 (25), 106 (20), 105 (26), 92 (33), 91 (100).

<sup>&</sup>quot;The product of Leriverend and Conia" is listed as the *trans* isomer. The above product is a mixture of *cis* and *trans* isomers. It has been separated into the pure isomers both of which analyze correctly. Unpublished information, Mr. William Whalley.

Samples of 12 in cyclohexane soln were heated at  $150^{\circ}$  in a series of sealed ampules. Analysis by GLC showed that the rate of conversion to 14 was dependent on the ampule rather than the time of heating.

5-Phenyl-1,3-cyclohexadiene (15). Heating a pentane soln (ca 5%) of 5 in a sealed tube for 20 h at 150° gave a single product which was isilated by preparative TLC (silica gel, n-hexane as eluant). The product was a color-less liquid, UV max (cyclohexane) 260 nm (4000); NMR (CCl<sub>4</sub>)  $\delta$  (m, 1H), 2·41 (m, 1H), 3·52 (m, 1H), 4·7 (m, 4H), 7·2 (s, 5H). (Found: C, 92·15; H, 7·74. Calc. for C<sub>12</sub>H<sub>12</sub>: C, 92·26; H, 7·74%).

Compound 15 (23.4 mg) and 234 mg Pd-C were heated 30 min at 185° in a sealed tube. The mixture was taken up in ether and the catalyst was removed by filtration. Evaporation gave a white solid, 22 mg (93%), m.p. 67-68°; UV max (cyclohexane) 248 nm (14,000) [lit. values for biphenyl<sup>41</sup> are m.p. 69-70°, UV max (n-hexane) 246 (20,000)].

When 15 was heated at  $195^{\circ}$  for 3-4 h in a sealed tube under N<sub>2</sub>, a new compound (16) was obtained, UV max 303 nm (30,000).

5-(p-Chlorophenyl)-1-3-cyclohexadiene (17). A soln containing 50-60 mg of 7 in 6 ml pentane was heated in a sealed tube at 150° for 6 h. The main product was isolated by preparative TLC (silica gel, pentane as eluant), UV max 252 nm (4900), NMR (CCL)  $\delta$  2·40 (m, 2H), 3·50 (m, 1H), 5·80 (m, 4H), 7·15 (s, 4H). (Found: C, 75·72; H, 5·77. Calc. for C<sub>12</sub>H<sub>11</sub>Cl: C, 75·59; H, 5·82%).

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