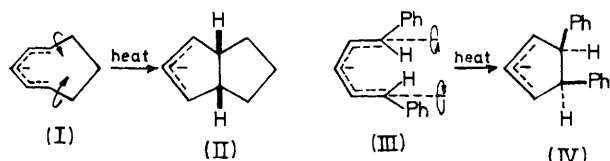


## Electrocyclic Reactions. Part VI.<sup>1</sup> Thermal Reactions of 1,5-Diphenylpentadienide Ion and the Anions derived from *cis*- and *trans*-3,4-Diphenylcyclopentene <sup>2</sup>

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Thermal cyclisation of the anion derived from the stereoisomeric 1,5-diphenylpenta-1,4-dienes could not be effected in 2,5,8-trioxanonane (diglyme) at 160° or in decalin at 190°, but has been achieved by Wolff–Kishner reaction of the semicarbazone of *trans,trans*-dibenzylideneacetone with powdered potassium *t*-butoxide at 225°, to give *cis*-3,4-diphenylcyclopentene. In all such Wolff–Kishner reactions *trans*-3,4-diphenylcyclopentene was also formed, and was the major product when solid sodium methoxide and potassium hydroxide were used as reagents; 1,5- and 1,2-diphenylcyclopentene were also produced. Thermal cycloreversion of the anions derived from *cis*- and *trans*-3,4-diphenylcyclopentene could not be effected in diglyme at 160° or in decalin at 190°; instead, the *cis*-material was isomerised to 1,5-diphenylcyclopentene (89% in diglyme, 56% in decalin), but the *trans*-substance was essentially not isomerised (2–3% in diglyme, 0% in decalin). With powdered potassium *t*-butoxide at 225° both *cis*- and *trans*-materials were isomerised to a mixture of 1,5- and 1,2-diphenylcyclopentene (*ca.* 1 : 5).

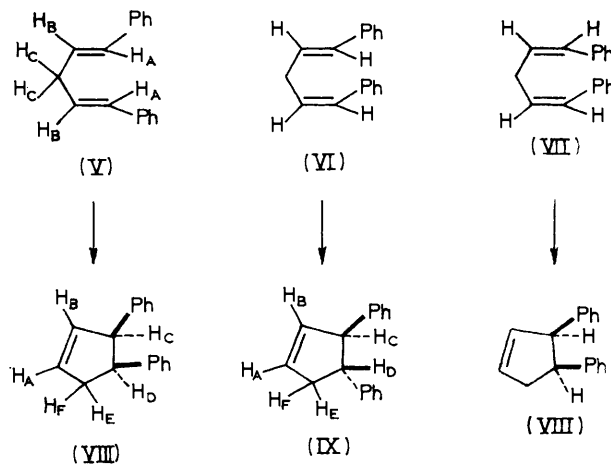
THE only recorded example of the thermal electrocyclic cyclisation of a pentadienide ion to give a cyclopentide ion is the disrotatory conversion<sup>3</sup> of the cyclo-octadienide ion (I) to the *cis*-bicyclo[3.3.0]octenide ion (II). We now describe the thermal disrotatory electrocyclic cyclisation of 1,5-diphenylpentadienide ion (III) to *cis*-4,5-diphenylcyclopentenide ion (IV).



Concerted thermal ground state electrocyclic reactions of the anions of *trans,trans*- (V), *cis,trans*- (VI), and *cis,cis*-1,5-diphenylpenta-1,4-diene (VII) are symmetry-allowed six-electron [ $\pi 2_s + \omega 2_s + \pi 2_s$ ] disrotatory processes,<sup>4</sup> which should furnish the anions of *cis*- (VIII), *trans*- (IX), and *cis*-3,4-diphenylcyclopentene (VIII), respectively. However, Brenner and Klein have reported<sup>5</sup> that treatment of a mixture of the 1,4-dienes (V)–(VII), or a mixture of the isomeric 1,5-diphenylpenta-1,3-dienes,<sup>6</sup> with *n*-butyl-lithium in ether gave a single pentadienide ion, whose <sup>1</sup>H n.m.r. spectrum was unchanged after 5 days at 38° and unaltered after heating to 70°. We have extended these observations.

The isomeric pentadienes (V)–(VII) were prepared by the method of Wittig *et al.*<sup>7</sup> from the bis-ylide of trimethylene-1,3-bis(triphenylphosphonium) dibromide and benzaldehyde.<sup>5,8</sup> We hoped by reduction of *trans,trans*-dibenzylideneacetone with lithium aluminium hydride–aluminium chloride in ether at 25° to obtain only the *trans,trans*-diene (V); g.l.c. of the product disclosed the production of one stereoisomer (V) ( $M^+$

220), but also the formation of two isomeric dihydrocompounds, C<sub>17</sub>H<sub>18</sub> ( $M^+$  222), probably *cis*- and *trans*-1,5-diphenylpent-1-ene, by 1,4-reduction. We attempted to achieve cyclisation of the pentadienide anion, corresponding to the reactions (V) → (VIII), (VI) → (IX), and (VII) → (VIII), by working at 160 and 190°. Generation of the anion derived from the pentadienes (V)–(VII) with sodamide or with *n*-butyl-lithium in diglyme (2,5,8-trioxanonane) and extended heating at 160° failed to yield, after quenching, either of the cyclopentenones (VIII) and (IX) as shown by g.l.c., and



gave intractable polymers of unknown structure. Use of *n*-butyl-lithium in decalin at 190° led to the same result.

We do not think that failure to cyclise under the above conditions is to be attributed to conformational factors or to adverse thermodynamics. Brenner and Klein<sup>5</sup> state that their <sup>1</sup>H n.m.r. data are consistent with an all-*trans*-configuration of the 1,5-diphenylpentadienide ion, but do not exclude other configurations

<sup>5</sup> S. Brenner and J. Klein, *Israel J. Chem.*, 1969, **7**, 735; *cf.* H. Yasuda, T. Narita, and H. Tani, *Tetrahedron Letters*, 1973, 2443.

<sup>6</sup> H. Stertter and A. Reichl, *Chem. Ber.*, 1960, **93**, 791.

<sup>7</sup> G. Wittig, H. Eggers, and P. Duffner, *Annalen*, 1958, **619**, 10.

<sup>8</sup> E. Block and H. W. Orf, *J. Amer. Chem. Soc.*, 1972, **94**, 8438.

<sup>1</sup> Part V, C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1974, 189.

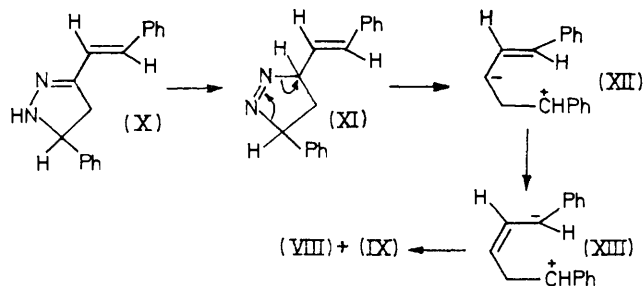
<sup>2</sup> C. W. Shoppee and G. N. Henderson, *J.C.S. Chem. Comm.*, 1974, 561.

<sup>3</sup> R. B. Bates and D. A. McCombs, *Tetrahedron Letters*, 1967, 977; *cf.* L. H. Slaugh, *J. Org. Chem.*, 1967, **32**, 108.

<sup>4</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, pp. 45, 70; *J. Amer. Chem. Soc.*, 1965, **87**, 395; H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, p. 2045.

(compare refs. 9–12). The 1,5-diphenylpentadienide ion can assume ten planar conformations [H/H: *tttt*, *tttc*, *tctt*, *ttcc*, *tcct*, *tctc*, *cctc*, *ccct*, *cccc* (*c* = *cis*, *t* = *trans*)], of which three (*ttcc*, *ccct*, and *cctc*) show large Ph/H steric interactions, and one (*cccc*) [cf. (VII)] appears sterically impossible on account of an insuperable Ph/Ph interaction. The U-shaped *tctc*-conformation [cf. (V)] appears capable of existence and of undergoing a thermal disrotatory electrocyclic reaction to give, after protonation, *cis*-3,4-diphenylcyclopentene (VIII); one of the less sterically probable U-shaped conformations (*ccct*) [cf. (VI)] also appears capable of existence and of a disrotatory electrocyclic reaction to give, after protonation, *trans*-3,4-diphenylcyclopentene (IX). To test the existence of a possible adverse thermodynamic situation, we prepared the *cis*- and *trans*-3,4-diphenylcyclopentenes (VIII) and (IX), and investigated the thermal behaviour of their anions in diglyme at 35 and 160°, and in decalin at 190°.

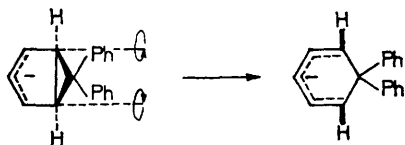
*trans*-3,4-Diphenylcyclopentene (IX) was prepared by the method of Kishner.<sup>13</sup> *trans,trans*-Dibenzylideneacetone and hydrazine gave the  $\Delta^2$ -pyrazoline (X), which was isomerised to the  $\Delta^1$ -pyrazoline (XI). Thermal decomposition of the latter by way of the zwitterion<sup>14</sup> (XII)  $\longleftrightarrow$  (XIII), or the corresponding diradicals,<sup>15</sup> furnished the *trans*-cyclopentene (IX) (91%), whose structure was confirmed by its <sup>1</sup>H n.m.r. spectrum and by hydrogenation to *trans*-1,2-diphenylcyclopentane.<sup>16</sup> G.l.c. analysis of the product showed the presence, as a result of some loss of stereochemistry in the intermediate (XIII), of the isomeric *cis*-cyclopentene (VIII) (9%), which was not observed by Kishner;<sup>13</sup> this was



isolated by preparative g.l.c. and its structure confirmed by its <sup>1</sup>H n.m.r. spectrum and by hydrogenation to *cis*-1,2-diphenylcyclopentane.<sup>16</sup>

*trans*-3,4-Diphenylcyclopentene (IX) with *n*-butyl-

\* A concerted thermal symmetry-allowed disrotatory carbanionic cyclopentenide-pentadienide cycloreversion has recently been described,<sup>17</sup> in which the driving force is relief of strain in the bicyclic structure.



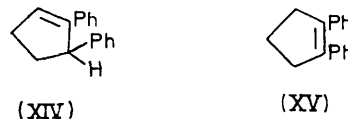
<sup>9</sup> R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, 1963, **85**, 3031.

<sup>10</sup> R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, 1966, **88**, 943.

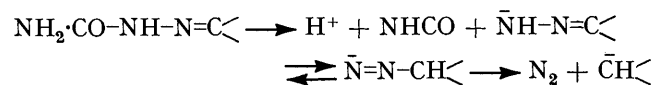
<sup>11</sup> G. J. Heiszwolf and H. Kloosterziel, *Rec. Trav. chim.*, 1967, **86**, 807.

lithium in diglyme at 35° gave an immediate blue colour; after 24 h analytical g.l.c. of the protonated product showed the presence only of the starting material (IX); this was isolated by preparative g.l.c. and its identification confirmed by its <sup>1</sup>H n.m.r. spectrum. With sodamide in refluxing diglyme as reagent at 160° for 6 days, analytical g.l.c. of the protonated product showed the presence only of starting material (IX). With *n*-butyl-lithium under the same conditions two peaks were observed, one corresponding to starting material (IX), and one shown to be due to traces of 1,5-diphenylcyclopentene (XIV) (2.6, 2.9, and 3.3%) (see later). The *trans*-hydrocarbon (IX) was unchanged by extended treatment with *n*-butyl-lithium in decalin at 190°. *cis*-3,4-Diphenylcyclopentene (VIII), with *n*-butyl-lithium in refluxing diglyme at 160° for 6 days and after protonation of the product, gave starting material (VIII) and 1,5-diphenylcyclopentene (XIV) (89%) (g.l.c.); a similarly extended reaction in decalin at 190° gave starting material (VIII) and 1,5-diphenylcyclopentene (XIV) (56%). *n*-Butyl-lithium appears to be a stronger base in diglyme than in the aprotic medium decalin, probably on account of solvation of the lithium cation. No thermal symmetry-allowed disrotatory cycloreversion to the 1,5-diphenylpentadienide ion (III) was detected in these experiments.\*

The structure of 1,5-diphenylcyclopentene (XIV) was established by its <sup>1</sup>H n.m.r. and mass spectra, and by hydrogenation to *cis*-1,2-diphenylcyclopentane.<sup>16</sup> We attribute the isomerisation of the *cis*-3,4-diphenylcyclopentene (VIII) to the 1,5-diphenyl derivative (XIV) to ready abstraction of the allylic C-3 proton by base followed by protonation at C-1. Conversely, we attribute the failure of the *trans*-3,4-diphenylcyclopentene (IX) to undergo effective isomerisation to (XIV) to steric hindrance by the 4-phenyl group preventing extraction of the eclipsed allylic C-3 proton.



We believe that polymerisation excludes cyclisation of the 1,5-diphenylpentadienide ion (III) under the conditions cited above. We therefore generated the 1,5-diphenylpentadienide ion *in situ* at 225° by use of the Wolff-Kishner reaction:<sup>18</sup>



<sup>12</sup> R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 1967, 199, 205; cf. W. T. Ford, and M. Newcomb, *J. Amer. Chem. Soc.*, 1974, **96**, 309.

<sup>13</sup> N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 958 (*Chem. Z.*, 1913, II, 2130).

<sup>14</sup> B. P. Stark and A. J. Duke, 'Extrusion Reactions,' Pergamon, 1967, p. 116 *et seq.*

<sup>15</sup> A. N. Kost and V. V. Ershov, *Uspekhi Khim.*, 1958, **27**, 431, esp. pp. 452, 453.

<sup>16</sup> H. A. Weidlich, *Ber.*, 1938, **71**, 1601.

<sup>17</sup> M. J. Perkins, and P. Ward, *J.C.S. Perkin I*, 1974, 667.

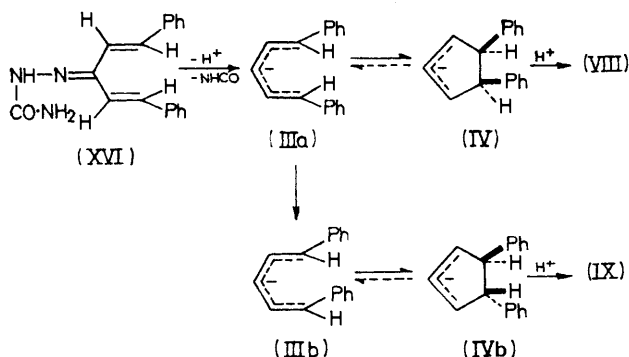
<sup>18</sup> D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, 1963, **85**, 1108; H. H. Szmant, *Angew. Chem.*, 1968, **80**, 141.

Treatment of *trans,trans*-dibenzylideneacetone semicarbazone<sup>19,20,21</sup> (XVI) at 225° and 2 mmHg with powdered potassium t-butoxide, sodium methoxide, or potassium hydroxide gave *cis*- and *trans*-3,4-diphenylcyclopentene, (VIII) and (IX), and the cyclopentene isomers (XIV) and (XV) as the only volatile products (apart from t-butyl alcohol). The products were isolated by g.l.c. and identified by comparison of their retention times, <sup>1</sup>H n.m.r. spectra (see Figures 1 and 2), and mass spectra with those of the synthetic compounds. The results are given in the Table. There may be some

Cyclisation products from the semicarbazone (XVI) at 225°

Base	(VIII) (%)	(IX) (%)	(XIV) and (XV) (%)
KOBu <sup>t</sup>	7	25	68
NaOMe	23	73	4
KOH	17	74	9

loss of stereochemistry in the anion (IIa) with potassium t-butoxide and appreciable loss with sodium methoxide



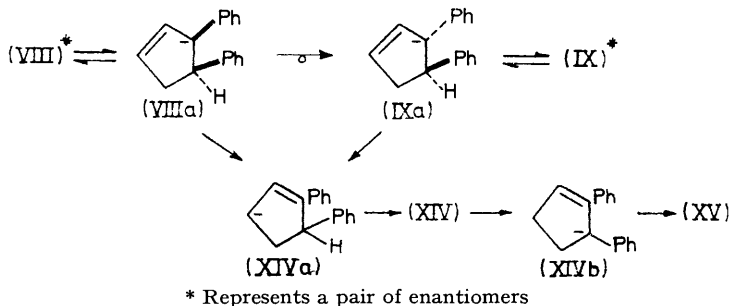
and potassium hydroxide leading *via* the anion (IIIb) to the *trans*-4,5-diphenylcyclopentenide ion (IVb) and production of *trans*-3,4-diphenylcyclopentene (IX). An alternative view is, however, possible: *cis*-3,4-diphenylcyclopentene (VIII) may be the sole initial cyclisation product. We find that with powdered potassium t-butoxide at 225° both the *cis*- (VIII) and the *trans*-3,4-diphenylcyclopentene (IX) undergo conversion into the conjugated isomers (XIV) and (XV), so that the *trans*-hydrocarbon (IX) isolated may be derived from the initially formed *cis*-hydrocarbon (VIII). These conditions do not exactly reproduce those of the semicarbazone-potassium t-butoxide melt in the Wolff-Kishner reaction, but we can no longer suggest, as in our preliminary communication,<sup>2</sup> that the initial yields of the *cis*-isomer (VIII) should be 75, 27, and 26% rather than 7, 23, and 17% as given in the Table; that a mixture of the cyclopentenes (VIII), (IX), (XIV), and (XV) is observed in the Wolff-Kishner reaction is probably because they are rapidly removed from the reaction site by distillation.

We consider that the simplest interpretation of the results involves the occurrence of a thermal symmetry-allowed [ $\pi 2_s + \omega 2_s + \pi 2_s$ ] disrotatory electrocyclic process (IIIa)  $\rightarrow$  (IVa)  $\rightarrow$  (VIII). Production of the

<sup>19</sup> G. Knöpfer, *Monatsh.*, 1911, **32**, 764.

<sup>20</sup> I. Mazurewitsch, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 19 (*Chem. Z.*, 1926, I, 913).

conjugated isomers (XIV) and (XV) appears to depend on the generation of t-butyl alcohol simultaneously with, and in the vicinity of, the carbanions (VIIIa), (IXa), and (XIVa); t-butyl alcohol then serves as a proton source for the base-catalysed conversions (VIIIa)  $\rightarrow$  (XIV), (IXa)  $\rightarrow$  (XIV), and (XIVb)  $\rightarrow$  (XV).



When the semicarbazone (XVI) was heated with a solution of sodium in the protic solvent diethylene glycol at 245°, or with powdered potassium t-butoxide in the aprotic solvent decalin at 190°, no cyclisation occurred, and the main product, isolated by g.l.c., was *trans,trans*-1,5-diphenylpenta-1,3-diene,<sup>6</sup> whose <sup>1</sup>H n.m.r. spectrum in deuteriochloroform was practically identical with that in dimethyl sulphoxide depicted by Brenner and Klein.<sup>5</sup> This result contrasts with the formation of cyclic products in the potassium t-butoxide-semicarbazone melt of the Wolff-Kishner reaction and may imply that separation of the potassium cation and the 1,5-diphenylpentadienide ion (IIIa) may be an important factor; alternatively, in the melt the anion (IIIa) may be formed in a high-energy state, whilst in the presence of solvent the anion (IIIa) may be in a relatively low-energy state as a result of transfer of energy to the solvent.

#### EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Thomas hot-stage apparatus and are corrected. I.r. spectra (solutions in carbon tetrachloride) were measured with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were measured with Varian A60 and XL100-15 instruments for solutions in deuteriochloroform (unless otherwise stated) with tetramethylsilane as internal reference. Mass spectra were measured with a Varian-MAT 311 double-focus spectrometer. Column chromatography was performed using aluminium oxide (Woelm; neutral). T.l.c. was carried out using silica gel G (Merck); plates were developed by exposure to iodine vapour. G.l.c. was carried out with a Varian Aerograph 1520 instrument fitted with flame ionisation and thermal conductivity detectors using analytical 5 ft  $\times$  1/4 in columns packed with 5% SE30 on Chrom G (60–80 mesh) [column (A)], or a preparative 20 ft  $\times$  5/8 in column packed with 20% SE30 on Chrom W (45–60 mesh) [column (B)].

1,5-Diphenylpenta-1,4-dienes [(V)–(VII)].—(a) The procedure of Wittig *et al.*,<sup>7</sup> with trimethylene-1,3-bis(tri-phenylphosphonium) dibromide [58 g; m.p. 335° (decomp.)],

<sup>21</sup> H. Stobbe and K. Bremer, *J. prakt. Chem.*, 1929, **123**, 241, 248.

*n*-butyl-lithium, and benzaldehyde in ether at 35°, gave a product (21.6 g;  $\nu_{\max}$ . 982 and 960  $\text{cm}^{-1}$ ), which by column chromatography on aluminium oxide in hexane (elution with benzene) gave a pale yellow oil (9.9 g),  $\nu_{\max}$ . 978 vs  $\text{cm}^{-1}$  (*trans*-CH=CH). The  $^1\text{H}$  n.m.r. spectrum,  $\delta$  2.9—3.6 (2H, m,  $\text{H}_C$ ), 5.5—6.6 (4H, m,  $\text{H}_A$  and  $\text{H}_B$ ), and 7.2 (10H, m, ArH), appeared to be a superposition of the spectra  $^{5,8}$  of the dienes (V)—(VII) (Found: C, 92.65; H, 7.3;  $M^+$ , 220. Calc. for  $\text{C}_{17}\text{H}_{16}$ : C, 92.7; H, 7.3%;  $M$ , 220). In a repetition, g.l.c. analysis of the crude product on column (A) at 245° gave five major peaks, and a mass spectrum showed  $m/e$  212, 220, and 278. The components were separated by preparative g.l.c. on column (A) at 230° and their mass spectra recorded: (i)  $M^+$  212, benzoin; (ii)  $M^+$  220, diene (VII); (iii)  $M^+$  220, diene (VI); (iv)  $M^+$  220, diene (V); (v)  $M^+$  278, triphenylphosphine oxide. Column chromatography on aluminium oxide in hexane with benzene as eluant led to isomerisation as disclosed by g.l.c.; peak (ii) was reduced in size, peak (iii) almost vanished, and peak (iv) was enlarged. Distillation gave a main fraction, b.p. 120—150° at 0.5 mmHg, shown by mass spectrometry to contain the dienes with  $M^+$  220; a highly viscous yellow residue remained.

(b) Purified trimethylene-1,3-bis(triphenylphosphonium) dibromide [58 g; m.p. 348—350° (decomp.) (from ethanol); lit., $^{7,8}$  333—335° (decomp.)] was treated successively with *n*-butyl-lithium and benzaldehyde as in (a). Distillation of the product gave a major fraction, b.p. 120—140° at 0.5 mmHg (7.3 g), g.l.c. analysis of which on column (A) at 247° showed the presence of three components: (i)  $t_R$  3.2 min, (VII); (ii)  $t_R$  4.0 min, (VI); (iii)  $t_R$  4.4 min, (V). Brenner and Klein $^5$  and Block and Orf $^8$  report the same elution sequence [ $t_R$ : (VII) > (VI) > (V)]. The three dienes could be separated by preparative g.l.c. on column (A) at 235°, but the mixture (V)—(VII) was used in subsequent experiments.

(c) Lithium aluminium hydride (10.3 g) was added slowly with cooling and stirring to anhydrous aluminium chloride (72.5 g) in ether (480 ml) under nitrogen; *trans,trans*-dibenzylideneacetone (40 g) dissolved in ether-tetrahydrofuran (1:1; 800 ml) was added to the grey suspension, and the mixture was stirred overnight at 20°. The mixture was decomposed by cautious addition of water, and extracted with ether. T.l.c. of the product (36 g) on silica in benzene showed three components; rapid column chromatography on aluminium oxide (1 kg) in hexane (benzene as eluant) gave a pale yellow liquid, b.p. 130—134° at 1 mmHg, showing no i.r. carbonyl absorption. G.l.c. on column (A) at 250° disclosed three major peaks, and a mass spectrum showed peaks at  $m/e$  220 and 222. The three components were separated by preparative g.l.c. on column (B) at 235°, and their mass spectra were recorded: (i)  $t_R$  7.3 min,  $M^+$  222,  $\text{C}_{17}\text{H}_{18}$ ; (ii)  $t_R$  9.6 min,  $M^+$  222,  $\text{C}_{17}\text{H}_{18}$ ; (iii)  $t_R$  13.5 min,  $M^+$  220,  $\text{C}_{17}\text{H}_{16}$ , *trans,trans*-1,5-diphenylpenta-1,4-diene (V), although further g.l.c. analysis, on Carbowax 20M and Apiezon L columns, indicated the presence of a trace of one or other of the isomers (VI) and (VII). The fragmentation patterns of the two compounds  $\text{C}_{17}\text{H}_{18}$  were identical except for small differences in the relative intensities of certain peaks:  $m/e$  131 ( $+\text{CH}_2\text{-CH}_2\text{-CH=CHPh}$ ), 117 ( $+\text{CH}_2\text{-CH=CHPh}$ ), 103 ( $+\text{CH=CHPh}$ ), and 91 ( $+\text{CH}_2\text{Ph}$ ), suggesting that these compounds are probably *cis*- and *trans*-1,5-diphenylpent-1-ene.

*Reactions of the 1,5-Diphenylpenta-1,4-dienes* (V)—(VII).

—(a) The mixed dienes [4 g from preparation (a)], dis-

solved in diglyme (10 ml), were added to sodamide (0.7 g) stirred in diglyme (50 ml) under nitrogen. At 130° after 15 min the solution became dark blue and ammonia was evolved; after heating at 130° for 3 days, the dark brown mixture was cooled, ice and water were added, and the product was extracted with ether. A solution of the product in benzene was filtered through a short column of aluminium oxide, and evaporated; the residue, which did not show an i.r. peak at 980  $\text{cm}^{-1}$  (*trans*-CH=CH), was rubbed with hexane and cooled to give a crystalline dimer,  $(\text{C}_{17}\text{H}_{16})_2$ , m.p. ca. 95°,  $M^+$  440, which was filtered off. The filtrate was chromatographed on silica in carbon tetrachloride; the first eluate was rejected and the second and third eluates were evaporated and united to yield a viscous pale yellow liquid containing polymers [Found: C, 92.7; H, 7.3. Calc. for  $(\text{C}_{17}\text{H}_{16})_n$ : C, 92.6; H, 7.3%]. In a repetition, the mixed dienes [0.6 g from preparation (b)] after heating at 160° for 6 days yielded a product, which by g.l.c. analysis on column (A) at 215° was shown to contain neither *cis*- (VIII) nor *trans*-3,4-diphenylcyclopentene (IX) ( $t_R$  6.8 and 7.8 min; see later); the starting dienes had been converted into polymers.

(b) The mixed dienes [0.3 g, from preparation (b)], dissolved in diglyme (10 ml; dried over lithium aluminium hydride) under nitrogen, were treated with 1.6M-*n*-butyl-lithium in hexane (1.5 ml). The solution became deep bluish violet, and was refluxed at 160° for 6 days. The dark brown mixture was cooled and acetic acid (2 ml) and an excess of water were added. The product, isolated with ether, was shown by g.l.c. analysis on column (A) at 215° to contain neither *cis*- (VIII) nor *trans*-3,4-diphenylcyclopentene (IX); the starting dienes had been converted into polymers.

(c) The mixed olefins [0.3 g, from preparation (b)], dissolved in decalin (10 ml) under nitrogen, were treated with 1.6M-*n*-butyl-lithium in hexane (1.5 ml). The red solution was refluxed at 190° for 6 days, and the dark brown mixture worked up as above. G.l.c. analysis on column (A) at 215° showed that neither *cis*- (VIII) nor *trans*-3,4-diphenylcyclopentene (IX) had been formed and that the starting dienes had been converted completely into polymers.

*cis- and trans-3,4-Diphenylcyclopentene* [(VIII) and (IX)]. —Dibenzylideneacetone (m.p. 111°; 58.5 g), dissolved in ethanol-ether (580 ml; 1:5), was treated dropwise at 0° with stirring with 100% hydrazine (12.5 ml) during 15 min; the mixture was allowed to warm to 20° (1.5 h) and stirred for a further 3 h. Solvents were removed to yield a semi-solid, which was heated at 250° for 1.5 h, and the product was distilled at 0.5 mmHg to yield four fractions:  $F_1$ , b.p. 108—124° (3.9 g);  $F_2$ , b.p. 124—136° (23 g);  $F_3$ , b.p. 136—148° (small); and  $F_4$ , b.p. 148—160° (small, yellow). G.l.c. analysis of  $F_2$  on column (A) at 215° gave three peaks: (i)  $t_R$  7.0 min (5%); (ii)  $t_R$  8.2 min (77%); (iii)  $t_R$  9.2 min (17%); g.l.c. analysis at 270° showed that fractions  $F_3$  and  $F_4$  contained high-boiling contaminants and these were rejected. Preparative g.l.c. of fraction  $F_2$  on column (B) at 246° (helium flow rate 71 ml  $\text{min}^{-1}$ ) enabled collection of the constituents of peaks (i) and (ii) and determination of their mass spectra: (i)  $t_R$  40 min, *cis*-3,4-diphenylcyclopentene (VIII) (6%) (Found:  $M^+$ , 220.1244.  $\text{C}_{17}\text{H}_{16}$  requires  $M$ , 220.1252),  $m/e$  220 (67%), 142 (18), 129 ( $M - \text{CH}_2\text{Ph}$ , base peak), 128 (33), 115 (27), 92 (27), 91 ( $+\text{CH}_2\text{Ph}$ , 23%), and 77 ( $\text{Ph}^+$ , 6%); for  $^1\text{H}$  n.m.r. spectrum see Figure 1; hydrogenated with 10% Pd-C in methanol to *cis*-1,2-diphenylcyclopentane, m.p. 45° (from ethanol) (lit., $^{18}$  45—46°),  $\delta$  2.10 (6H, unresolved m), 3.44

(2H, unresolved m), and 6.95br<sup>22,23</sup> (10H, m, ArH); (ii)  $t_R$  44.7 min, *trans*-3,4-diphenylcyclopentene<sup>13</sup> (IX) (77%) (Found:  $M^+$ , 220-1244. Calc. for  $C_{17}H_{16}$ :  $M$ , 220-1252),  $m/e$  220 (44%), 142 (23), 129 ( $M - CH_2Ph$ , base peak), 128 (37), 115 (40), 92 (43), 91 ( $+CH_2Ph$ , 42), and 77 ( $Ph^+$ , 16%); for  $^1H$  n.m.r. spectrum see Figure 2;

7 : 93. The constituents of peak (iii) were not investigated because its two constituents were only partially resolved on column (B) at 246°.

*Attempted Cycloversion of cis-3,4-Diphenylcyclopentene (VIII).*—(a) *cis*-3,4-Diphenylcyclopentene (100 mg), dissolved in diglyme (6.5 ml) under nitrogen, was treated with

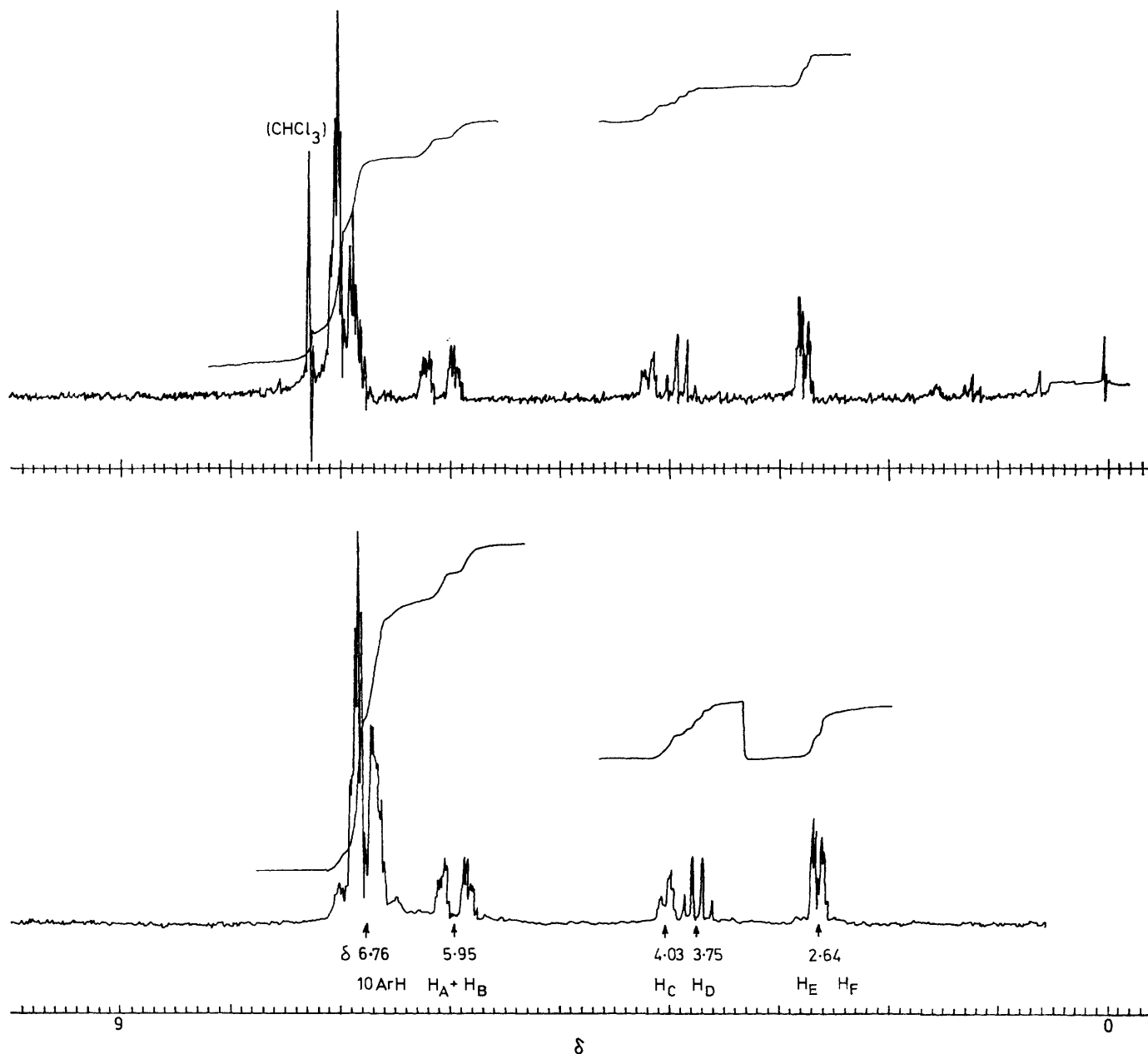


FIGURE 1 100 MHz  $^1H$  N.m.r. spectra of *cis*-3,4-diphenylcyclopentene (VIII): upper trace ( $CDCl_3$ ) as cyclisation product; lower trace ( $CCl_4$ ) as synthetic material;  $\delta$  2.64 (2H, 2q,  $H_E$ ,  $H_F$ ), 3.75 (1H, q,  $H_D$ ), 4.03 (1H, m,  $H_C$ ), 5.95 (2H 2 quint,  $H_A$ ,  $H_B$ ), and 6.76br<sup>22,23</sup> (10H, m, ArH)

hydrogenated with 10% Pd-C in methanol to *trans*-1,2-diphenylcyclopentane, m.p. 65° (from ethanol) (lit.,<sup>16</sup> 65°),  $\delta$  1.90 (6H, unresolved m), 2.92 (2H, unresolved m), and 6.94 (10H, narrow<sup>22,23</sup> m, ArH) (*cf.* ref. 24). The isomer ratios (VIII) : (IX) in fractions  $F_1$  and  $F_2$  were 18 : 82 and

<sup>22</sup> D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. and Ind.*, 1958, 1205.

<sup>23</sup> N. S. Bhacca, unpublished results.

1.6M-*n*-butyl-lithium in hexane (1 ml) with stirring. After 6 days at 160°, the brown solution was cooled, acidified with acetic acid, and diluted with water, and the product was extracted with ether. G.l.c. analysis on column (A) at 200° showed two peaks,  $t_R$  7.8 and 10.7 min, with relative

<sup>24</sup> L. Jackman and S. Sternhell, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Pergamon, 2nd edn., 1969, p. 274.

areas 11 and 89%; the components were separated by preparative g.l.c. on column (B) at 245°,  $t_R$  40 and 50.3 min, and their n.m.r. spectra determined. The spectrum of the minor product was identical with that of the starting

hydrogenated with 10% Pd-C in methanol to *cis*-1,2-diphenylcyclopentane<sup>16</sup> as the sole product, g.l.c. on column (A) at 210° giving a single peak,  $t_R$  6.25 min, as did g.l.c. on a 5 ft Carbowax 20 M column at 205° ( $t_R$

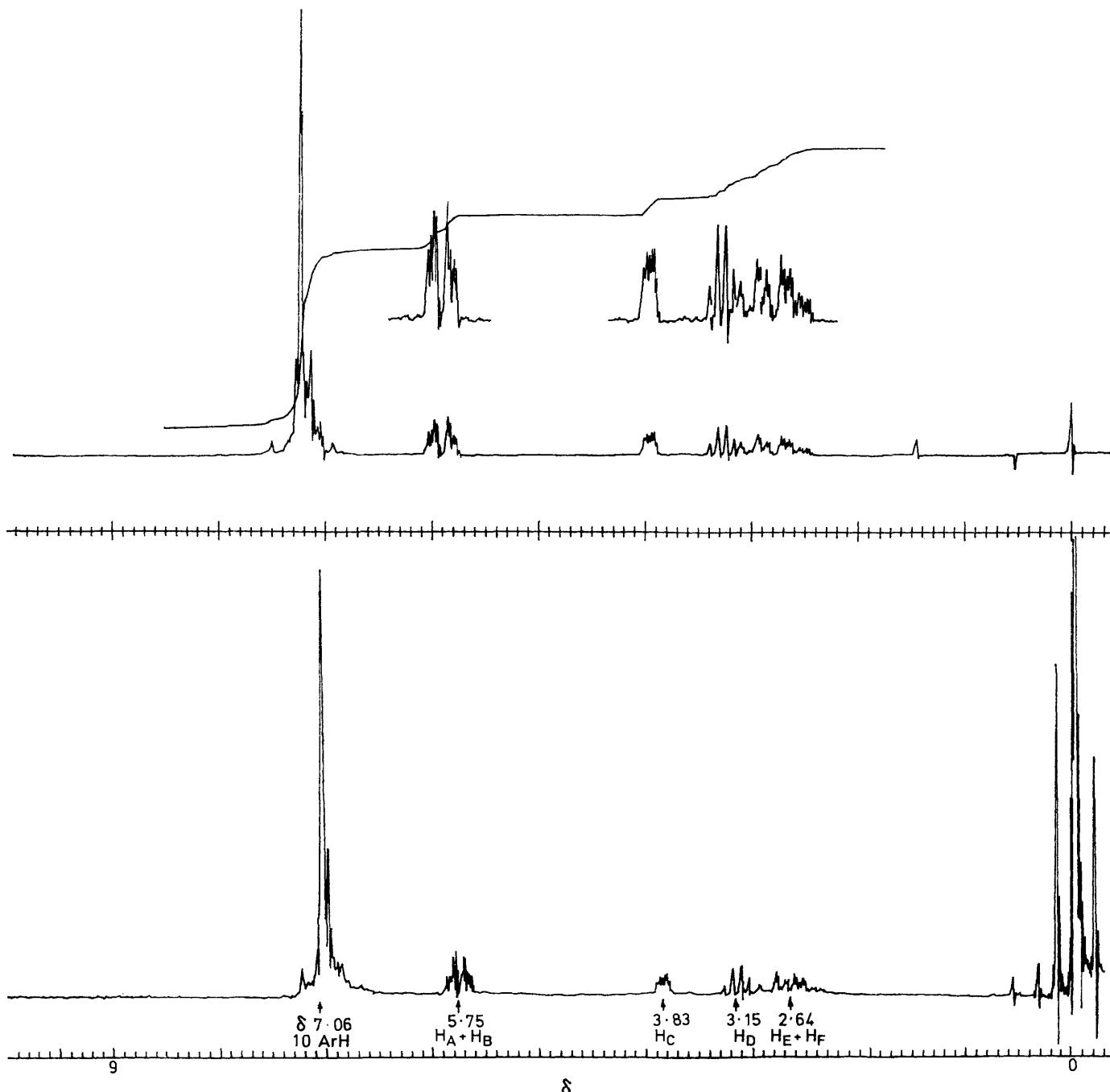


FIGURE 2 100 MHz  $^1\text{H}$  N.m.r. spectra of *trans*-3,4-diphenylcyclopentene (IX): upper trace ( $\text{CDCl}_3$ ) as cyclisation product; lower trace ( $\text{CDCl}_3$ ) as synthetic material;  $\delta$  2.64 (2H, 8 q,  $\text{H}_E$ ,  $\text{H}_F$ ), 3.15 (1H, q,  $\text{H}_D$ ), 3.83 (1H, octet,  $\text{H}_C$ ), 5.85 (2H, 2 quint,  $\text{H}_A$ ,  $\text{H}_B$ ), and 7.06 (10H, narrow  $^{22,23}$  m, ArH)

material; that of the major product showed it to be 1,5-diphenylcyclopentene (XIV),  $\delta$  2.54 (4H, m), 4.29 (1H, unresolved m), 6.44 (1H, q, vinyl), and 7.20 (10H, m, ArH) (Found:  $M^+$ , 220.1244.  $\text{C}_{17}\text{H}_{16}$  requires  $M$ , 220.1252),  $m/e$  220 (base peak), 219 (45%), 205 (22), 143 (26), 142 (50), 141 (22), 115 (41), 92 (22), and 91 ( $+\text{CH}_2\text{Ph}$ , 52);

7.2 min) on which the *cis*- and *trans*-1,2-diphenylcyclopentanes are well separated<sup>25</sup> ( $t_R$  7.2 and 7.8 min); the  $^1\text{H}$  n.m.r. spectrum,  $\delta$  2.10 (6H, m), 3.44 (2H, m), and 6.95br (10H, m, ArH) (*cf.* ref. 24), was identical with that of an<sup>25</sup> C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1972, 2271.

authentic sample obtained by hydrogenation of *cis*-3,4-diphenylcyclopentene.

(b) Experiment (a) was repeated in decalin (6.5 ml) at 190° for 6 days. G.l.c. analysis of the product on column (A) at 200° again showed two peaks (44 and 56%); the components were separated by preparative g.l.c. on column (B) at 245°, and identified by their <sup>1</sup>H n.m.r. spectra as *cis*-3,4-diphenylcyclopentene (VIII) and 1,5-diphenylcyclopentene (XIV).

*Attempted Cycloversion of trans-3,4-Diphenylcyclopentene* (IX).—(a) *trans*-3,4-Diphenylcyclopentene (0.3 g), dissolved in diglyme (10 ml) under nitrogen, and sodamide (0.1 g) were heated to 160°; ammonia was evolved and the solution became brown. After 5 days at 160°, the solution was cooled, acetic acid (0.2 ml) and an excess of water were added, and the product was extracted with ether. G.l.c. analysis on column (A) at 230° gave a single peak with the same retention time as the starting material; this was isolated by preparative g.l.c. on column (B) at 245° (*t*<sub>R</sub> 44.7 min) and its identification confirmed by its <sup>1</sup>H n.m.r. spectrum.

(b) Experiment (a) was repeated using 1.6M-n-butyl-lithium in hexane (1.5 ml); after 6 days at 160°, g.l.c. analysis of the product on column (A) at 200° showed two peaks, *t*<sub>R</sub> 9.5 and 10.7 min, with relative areas 97.4 : 2.6. Preparative g.l.c. on column (B) at 245° gave as the major constituent the starting material (IX) and as the minor constituent 1,5-diphenylcyclopentene (XIV), whose identities were confirmed by their <sup>1</sup>H n.m.r. spectra. In two repetitions, the proportions (IX) : (XIV) were 96.7 : 3.3 and 97.1 : 2.9.

(c) Experiment (b) was repeated in decalin (15 ml) at 190° for 6 days. G.l.c. analysis of the product on column (A) at 210° gave only a single peak with the same retention time as the starting material, isolated by preparative g.l.c. on column (B) at 245° and identified by its <sup>1</sup>H n.m.r. spectrum.

*trans,trans-Dibenzylideneacetone Semicarbazone* (XVI).—This was prepared from *trans,trans*-dibenzylideneacetone by treatment with a concentrated solution of semicarbazide acetate in acetic acid<sup>19</sup> at 25°, or in methanol containing a little toluene-*p*-sulphonic acid at 25°. The semicarbazone, after several recrystallisations from chloroform-ethanol, had m.p. 174.5° (lit.,<sup>19</sup> 187–190°; lit.,<sup>20</sup> 174°), and was identified by its <sup>1</sup>H n.m.r. spectrum: δ 5.69br (2H, s, NH<sub>2</sub>), 6.77 (1H, d, vinyl, *J* 16.5 Hz), 6.97 (2H, d, vinyl, *J* 16.25 Hz), 6.99 (1H, d, vinyl, *J* 16.5 Hz), 7.23–7.61 (10H, complex m, ArH), and 8.70 (1H, s, NH), δ (CD<sub>3</sub>CN) 5.74br (2H, s, NH<sub>2</sub>), 6.92 (1H, d, *J* 17 Hz), 7.06 (2H, t, *J* 17.5 Hz), 7.19 (1H, d, *J* 17 Hz), 7.26–7.68 (10H, complex m, ArH), and 8.56 (1H, s, NH), and by its mass spectrum: *m/e* 291 (*M*<sup>+</sup>), 290, 274, 248, 247, 246, 232, 231, 218, 171, 144, 130, 128, 115, 104, 102, 91, 77, 46, 45 (base peak, HCONH<sub>2</sub>), and 43, yielding a consistent fragmentation pattern (Found: C, 74.15; H, 6.0; N, 14.4%; *M*<sup>+</sup>, 291.1379. Calc. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O: C, 74.2; H, 5.9; N, 14.4%; *M*, 291.1372).

*Cyclisation of the 1,5-Diphenylpenta-1,4-dienide Ion*.—(a) *trans,trans*-Dibenzylideneacetone semicarbazone (XVI) (2 g) and potassium *t*-butoxide [2 g; powder (Aldrich)] were quickly and intimately mixed under dry nitrogen, and the mixture was rapidly heated to 225°; after 5 min the pressure was reduced to 2 mmHg and the distillate was collected for 10 min in a receiver immersed in freezing

mixture. The distillate (0.65 g) was found by g.l.c. and its <sup>1</sup>H n.m.r. spectrum to be mainly *t*-butyl alcohol containing *ca.* 200 mg of diphenylcyclopentenenes. Analytical g.l.c. on column (A) at 190° disclosed three peaks (7.4, 24.8, and 67.8%) other than that for *t*-butyl alcohol; these three components were separated by preparative g.l.c. on column (B) at 246°: (i) *t*<sub>R</sub> 40 min, *M*<sup>+</sup> 220.1265, <sup>1</sup>H n.m.r. spectrum identical with that of *cis*-3,4-diphenylcyclopentene (VIII); (ii) *t*<sub>R</sub> 44.7 min, *M*<sup>+</sup> 220.1266, <sup>1</sup>H n.m.r. spectrum identical with that of *trans*-3,4-diphenylcyclopentene (IX); (iii) *t*<sub>R</sub> 50.3 min, *M*<sup>+</sup> 220.1265, whose <sup>1</sup>H n.m.r. spectrum showed it to be a mixture of 1,5-diphenylcyclopentene (XIV) (43%) and 1,2-diphenylcyclopentene (XV) (57%); this was hydrogenated with 10% Pd-C in methanol to *cis*-1,2-diphenylcyclopentane,<sup>16</sup> m.p. and mixed m.p. 46°. The distillation residue was treated with water and extracted with ether; the extract yielded a brown semisolid (1.14 g), which by g.l.c. analysis on column (A) at 225° and by its <sup>1</sup>H n.m.r. spectrum was shown to contain neither 1,5-diphenylpentadienes nor diphenylcyclopentenenes.

(b) The semicarbazone (2 g) and sodium methoxide [2 g; powder (Fisher)] under nitrogen were heated at 225° for 30 min as in (a) to give mixed cyclopentenenes (0.21 g). Analytical g.l.c. on column (A) at 191° showed three peaks (23, 73, and 4%), separated by preparative g.l.c. on column (B) at 246°: (i) *t*<sub>R</sub> 40 min, *M*<sup>+</sup> 220.1265, <sup>1</sup>H n.m.r. spectrum identical with that of (VIII); (ii) *t*<sub>R</sub> 44.7 min, *M*<sup>+</sup> 220.1265, <sup>1</sup>H n.m.r. spectrum identical with that of (IX); (iii) *t*<sub>R</sub> 50.3 min, *M*<sup>+</sup> 220.1265, insufficient for <sup>1</sup>H n.m.r. spectrum, regarded as (XIV) or (XV) or a mixture of these.

(c) The semicarbazone (2 g) and powdered potassium hydroxide (3 g) under nitrogen were heated at 225° for 30 min as in (a) to give mixed cyclopentenenes (0.21 g). Analytical g.l.c. on column (A) at 190° showed three peaks (16.7, 73.9, and 9.4%), separated by preparative g.l.c. on column (B) at 246°: (i) *t*<sub>R</sub> 40 min, *M*<sup>+</sup> 220.1265, <sup>1</sup>H n.m.r. spectrum identical with that of (VIII); (ii) *t*<sub>R</sub> 44.7 min, *M*<sup>+</sup> 220.1265, <sup>1</sup>H n.m.r. spectrum identical with that of (IX); (iii) *t*<sub>R</sub> 50.3 min, *M*<sup>+</sup> 220.1265, whose <sup>1</sup>H n.m.r. spectrum showed it to be (XIV) mixed with a small amount of (XV).

*Reactions of the Semicarbazone* (XVI).—(a) The semicarbazone (2.9 g) was added to a solution of sodium (0.9 g) in diethylene glycol (25 ml) and the mixture was refluxed for 2 h. Analytical g.l.c. of the product (2.25 g) on column (A) at 225° gave a single large peak (*t*<sub>R</sub> 8.0 min); preparative g.l.c. on column (A) at 225° gave *trans,trans*-1,5-diphenylpenta-1,3-diene<sup>6</sup> (PhCH<sub>A</sub>=CH<sub>B</sub>-CH<sub>C</sub>=CH<sub>D</sub>-CH<sub>E</sub>H<sub>F</sub>Ph), *t*<sub>R</sub> 8.0 min, *M*<sup>+</sup> 220.1265 [*m/e* 142, 141, 131, 130, 129 (base peak), 128, 116, 115, 104, 103, 92, 91, 78, and 77], identified by its <sup>1</sup>H n.m.r. spectrum: δ 3.50 (d, 2 H<sub>E</sub>), 5.96 (sextet, 1 H<sub>D</sub>), 6.27 (q, 1 H<sub>C</sub>), 6.47 (d, 1 H<sub>A</sub>), 6.80 (q, 1 H<sub>B</sub>), 7.60 (10H, m, ArH), *J*<sub>AB</sub> 15, *J*<sub>BC</sub> 9, *J*<sub>CD</sub> 15, *J*<sub>DE</sub> 6.5 Hz; irradiation at the frequency of the H<sub>E</sub> doublet caused the H<sub>D</sub> sextet to collapse to a doublet, and irradiation at the frequency of the H<sub>D</sub> sextet caused the H<sub>E</sub> doublet to collapse to a singlet (*cf.* ref. 5). Diphenylcyclopentenenes were not present in the product.

(b) The semicarbazone (2 g) and potassium *t*-butoxide (powder; 3 g) in *p*-xylene (75 ml) (*cf.* refs. 26 and 27) under nitrogen were refluxed for 30 min. Decomposition of the orange precipitate with water gave only the unchanged semicarbazone. The experiment was repeated with refluxing for 5 days; the product, isolated in the usual way, was an

<sup>26</sup> M. F. Grundon, H. B. Henbest, and M. D. Scott, *J. Chem. Soc.*, 1963, 1855.

<sup>27</sup> D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Amer. Chem. Soc.*, 1962, **84**, 1734.

orange semisolid (0.92 g). G.l.c. analysis and the  $^1\text{H}$  n.m.r. spectrum showed the absence of 1,5-diphenylpentadienes and of diphenylcyclopentenes, and the presence of unchanged starting material and unidentified products.

(c) The semicarbazone (2 g), potassium *t*-butoxide (powder; 3 g), and decalin (50 ml; Eastman-Kodak; mixture of *cis*- and *trans*-isomers) under nitrogen were refluxed for 30 min. The  $^1\text{H}$  n.m.r. spectrum of the crude product (1 g) indicated formation of *trans,trans*-1,5-diphenylpenta-1,3-diene; analytical g.l.c. on column (A) at  $250^\circ$  disclosed two peaks,  $t_R$  3.9 (29%) and 11 min (72%), and at  $225^\circ$  the first peak had the same  $t_R$  value (8.0 min) as *trans,trans*-1,5-diphenylpenta-1,3-diene, whilst the second peak was partially resolved into two peaks representing polymers with much larger  $t_R$  values than any of the isomeric 1,5-diphenylpenta-1,5-dienes or diphenylcyclopentenes. Preparative g.l.c. at  $240^\circ$  gave *trans,trans*-1,5-diphenylpenta-1,3-diene, identified by its  $^1\text{H}$  n.m.r. and mass spectra ( $M^+$  220.1265).

*Reactions of cis- and trans-3,4-Diphenylcyclopentene [(VIII) and (IX)] with Potassium t-Butoxide at  $225^\circ$ .*—

(a) The *trans*-cyclopentene (IX) (200 mg) and powdered potassium *t*-butoxide (300 mg) under nitrogen were heated at  $225^\circ$  for 30 min. The mixture was cooled and treated

with an excess of water, and the product, isolated in the usual way with ether, was dried by azeotropic distillation with benzene. Analytical g.l.c. on column (A) at  $190^\circ$  gave a single peak; preparative g.l.c. on column (B) at  $246^\circ$  enabled separation of this product, which was shown to be a *ca.* 1 : 5 mixture of 1,5- (XIV) and 1,2-diphenylcyclopentene (XV) by its  $^1\text{H}$  n.m.r. spectrum.

(b) A mixture of *cis*- (VIII) and *trans*-3,4-diphenylcyclopentene (IX) (42 : 58; 100 mg) was heated with potassium *t*-butoxide at  $225^\circ$  as in (a). Similar isolation of the product gave a *ca.* 1 : 5 mixture of the isomeric cyclopentenes (XIV) and (XV) as indicated by its  $^1\text{H}$  n.m.r. spectrum.

We thank Dr. R. M. Starrett for performing the lithium aluminium hydride-aluminium chloride reduction of *trans,trans*-dibenzylideneacetone, and Professor N. S. Bhacca, Louisiana State University, for evaluation of the  $^1\text{H}$  n.m.r. coupling constants of compound (IX). One of us (G. N. H.) acknowledges the tenure of a Welch Post-doctoral Research Fellowship; the other (C. W. S.) acknowledges the support of the Robert A. Welch Foundation, Houston, Texas.

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