

## Electrocyclic Reactions. Part 11.<sup>1</sup> 1,5-Diphenylpentadienide

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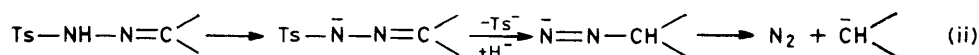
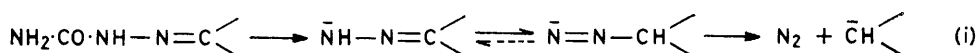
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1,5-Diphenylpentadienide, generated from *trans,trans*-dibenzylideneacetone *p*-tolylsulphonylhydrazone by the Caglioti reaction with lithium aluminium hydride, furnished *cis*-3,4-diphenylcyclopentenide, which by a supra-facial [1,4] sigmatropic shift and proton acquisition afforded 1,5-diphenylcyclopentene (18%); the other main products were toluene-*p*-sulphonamide and 1,5-diphenylpentan-3-imine (68%), formed by fission of the N-N bond of the sulphonyl hydrazone and reduction. Treatment of the sulphonylhydrazone with sodium methoxide in methanol thermally or photochemically yielded only 3(5)-phenyl-5(3)-styrylpyrazole. 3-Methoxy-1,5-diphenylpenta-1,4-diene with sodium-potassium alloy gave only *cis*- or *trans*-1,5-diphenylpent-2-ene.

1,5-DIPHENYLPENTADIENIDE can be produced from *trans,trans*-dibenzylideneacetone semicarbazone by the Wolff-Kishner reaction (i) and undergoes thermal cyclisation to *cis*-3,4-diphenylcyclopentene.<sup>2</sup> We have now examined other procedures expected to lead to the anion.

The Caglioti reaction<sup>3</sup> involves reduction of *p*-tolylsulphonylhydrazones with lithium aluminium hydride in

<sup>1</sup>H n.m.r. spectrum, which exhibits signals at  $\delta$  1.3 (NH), 1.7 (4 H<sub>A</sub>), 2.7 (4 H<sub>B</sub>), and 7.14 (10 aromatic protons). The product of primary interest was 1,5-diphenylcyclopent-1-ene (8), which showed <sup>1</sup>H n.m.r. signals at  $\delta$  2.4 (2H<sub>O</sub>), 2.6 (2 H<sub>D</sub>), 4.3 (H<sub>B</sub>), 5.45 (H<sub>A</sub>), and 7.2 (10 ArH) (*cf.* ref. 2, in which  $\delta$  6.44 should read  $\delta$  5.44). It appears to arise by loss of Ts<sup>-</sup> from the



aprotic solvents, and its mechanism (ii) has been demonstrated by deuterium labelling studies.<sup>4</sup>

Treatment of *trans,trans*-dibenzylideneacetone *p*-tolylsulphonylhydrazone (2) with lithium aluminium hydride in ether or tetrahydrofuran, followed by quenching with ice and aqueous ammonium chloride, gave the same three products in nearly the same proportions. Toluene-*p*-sulphonamide (3) and the imine (4) (65%) arise from the sulphonylhydrazone anion (2a) by fission of the N-N bond and reduction; the structure (4) † follows from the

sulphonylhydrazone anion (2a) and reduction to give the anion (1), which loses nitrogen to generate the 1,5-diphenylpentadienide anion (5); a thermal disrotatory [ $\pi 2_s + \pi 2_s$ ] cycloaddition then yields *cis*-3,4-diphenylcyclopentenide (6), which by a thermal symmetry-allowed suprafacial [1,4] sigmatropic shift<sup>5</sup> [ $\pi 4_s + \sigma 2_s$ ] gives the anion (7), the latter furnishing by proton acquisition 1,5-diphenylcyclopent-1-ene (8).

<sup>2</sup> C. W. Shoppee and G. N. Henderson, *J.C.S. Perkin I*, 1975, 765.

<sup>3</sup> L. Caglioti and M. Magi, *Tetrahedron*, 1963, **19**, 1127; L. Caglioti, *ibid.*, 1967, **22**, 487.

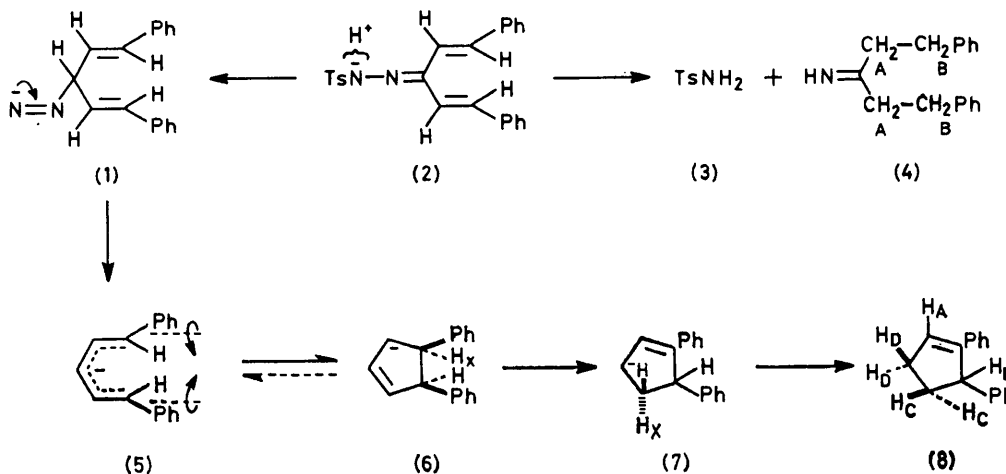
<sup>4</sup> M. Fischer, Z. Pelak, D. H. Williams, and C. Djerassi, *Chem. Ber.*, 1965, **98**, 3236; *cf.* I. Elphimoff-Felkin and M. Verrier, *Tetrahedron Letters*, 1968, 1515.

<sup>5</sup> R. E. Lehr and A. P. Marchand, 'Orbital Symmetry,' Academic Press, New York and London, 1972, p. 13.

† Because the structure of the product was revised to (4) after experimental work was completed, confirmation by hydrolysis to the related ketone was not carried out.

<sup>1</sup> Part 10, C. W. Shoppee, Y.-S. Wang, S. Sternhell, and G. C. Brophy, *J.C.S. Perkin I*, 1976, 1880.

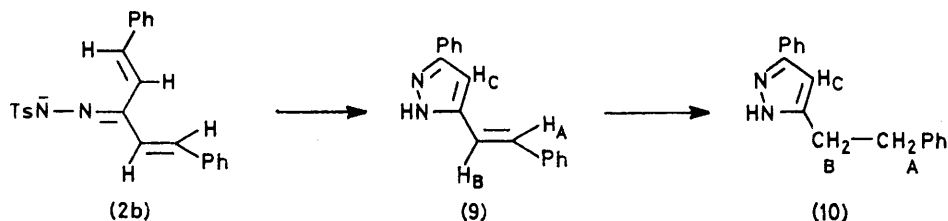
The Caglioti reaction in diethyl ether at 35 °C (or dioxan at 65 °C) for 44 h thus affords 1,5-diphenylcyclopentene (8), whereas the Wolff-Kishner fusion reaction with solid potassium t-butoxide at 225 °C and 2 mmHg for 5 min gave *cis*-3,4-diphenylcyclopentene [as (6)].



This suggests that, under the former conditions with the absence of protons, the anion (6) has a longer life and the opportunity to rearrange to the more thermodynamically stable conjugated anion (7).

Treatment of the sulphonylhydrazone (2) with sodium methoxide in methanol gave the anion (2a), which in the *s-cis,trans*-conformation (2b) yielded 3(5)-phenyl-5(3)-

(13) as the sole product, whose structure followed from its <sup>1</sup>H n.m.r. spectrum. G.l.c. confirmed the absence of *cis*-3,4-diphenylcyclopentene [as (6)] and 1,5-diphenylcyclopentene (8), the products also to be expected from [<sub>π</sub>2<sub>s</sub> + <sub>π</sub>2<sub>s</sub>] electrocycloislation of 1,5-diphenylpentadienyl (12) if this had been generated instead of the anion (5).

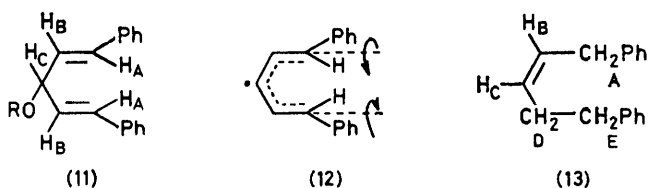


styrylpyrazole (9). This was hydrogenated over palladium in methanol to 3(5)-phenyl-5(3)-β-phenylethylpyrazole (10), which displayed a four-proton <sup>1</sup>H n.m.r. singlet at δ 2.9, owing to adventitious coincidence of the signals for H<sub>A</sub> and H<sub>B</sub>. The pyrazole (9) was the principal product of u.v. irradiation of a methanolic solution of the sulphonylhydrazone anion (2a).

#### 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. N.m.r. spectra were measured with a Varian XL 100-15 instrument for solutions in deuteriochloroform (unless otherwise stated) with tetramethylsilane as internal reference. Mass spectra were measured with a Varian-MAT 311 double-focus spectrometer. G.l.c. was carried out with a Varian Aerograph 1 520 instrument by using an analytical 5 ft × 1/4 in column packed with 5% SE30 on Chromosorb G (60–80 mesh) [column (A)], or a preparative 20 ft × 5/8 in column packed with 20% SE30 on Chromosorb W (45–60 mesh) [column (B)].

*trans,trans*-Dibenzylideneacetone *p*-Tolylsulphonylhydrazone (2).—This was best prepared by refluxing a solution of *trans,trans*-dibenzylideneacetone and *p*-tolylsulphonylhydrazine in ethanol with a catalytic amount of toluene-*p*-sulphonic or hydrochloric acid. The mixture was cooled to –10 °C, and the precipitated crystals were filtered off and washed with water. In a typical reaction, the ketone (2.34



Another attempt to generate 1,5-diphenylpentadienide (5) was made by application of the classical ether cleavage method of Ziegler and Schnell,<sup>7</sup> using sodium-potassium

<sup>6</sup> A. Dornow and W. Bartsch, *Annalen*, 1957, **602**, 23.

<sup>7</sup> K. Ziegler and B. Schnell, *Annalen*, 1924, **437**, 227.

<sup>8</sup> G. Hesse and P. Thieme, *Annalen*, 1965, **686**, 64.

<sup>9</sup> J. Sonderman and H. Kuhn, *Chem. Ber.*, 1966, **99**, 2491.

g) and the hydrazine (1.86 g), gave the *hydrazone* (2.61 g), m.p. 142–144° (decomp.) (from ethanol),  $\delta$  2.41 (3 H, s, CH<sub>3</sub>), 6.66 (1 H, d, vinylic,  $J$  16.75 Hz), 6.92 \* (1 H, d, vinylic,  $J$  16.75 Hz), 6.92 \* (2 H, t, vinylic,  $J$  17.75 Hz), 7.18 (12 H, complex m, 2 Ph and 2 ArH of Ts), 7.90 (2 H, d, 2 ArH of Ts,  $J$  8 Hz), and 8.22br (1 H, s, NH) (dilution shifted the NH signal to  $\delta$  8.04);  $\delta$  (CD<sub>3</sub>CN) 2.43 (3 H, s), 6.88 (1 H, d,  $J$  16.5 Hz), 6.90 (1 H, d,  $J$  16.25 Hz), 7.11 (1 H, d,  $J$  16.25 Hz), 7.13 (1 H, d,  $J$  16.5 Hz), 7.50 (12 H, m), and 7.87 (2 H, d,  $J$  8 Hz) (NH signal not observed);  $m/e$  402 ( $M^+$ , low intensity), 247, 246 (base peak), 245, 218, 217, 215, 202, 156, 143, 142, 116, 115, 104, 92, 91, 77, and 65 (Found: C, 71.9; H, 5.7; N, 6.8; S, 7.3%;  $M^+$ , 402.1442. C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 71.6; H, 5.5; N, 6.95; S, 7.95%;  $M$ , 402.1402).

*Caglioti Reaction of the Sulphonylhydrazone* (2).—(a) To a mixture of the sulphonylhydrazone (2 g) and lithium aluminium hydride (3 g), tetrahydrofuran (50 ml) was added with stirring at 25 °C; a vigorous reaction set in to give a green solution, which was refluxed and became blue. After 24 h ice-water was added and the solution was saturated with ammonium chloride and extracted with ether. The extract was evaporated, and the resultant oil (1.4 g) dried azeotropically with benzene. Analytical g.l.c. on column (A) at 230 °C disclosed three peaks, separated by preparative g.l.c. on column (B) at 230 °C to give: (i) toluene-*p*-sulphonamide (3) (9.7%),  $t_R$  3 min, m.p. and mixed m.p. 137°, whose <sup>1</sup>H n.m.r. spectrum was identical with that of an authentic specimen (Found:  $M^+$ , 171.132. Calc. for C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub>S:  $M$ , 171.1236); (ii) 1,5-diphenylcyclopentene (8) (18.4%),  $t_R$  4 min,  $\delta$  2.40 (m, 2 H<sub>C</sub>), 2.60 (m, 2 H<sub>D</sub>), 4.3 (m, H<sub>B</sub>), 5.55 (quint, vinylic H<sub>A</sub>), and 7.2 (m, 10 ArH),  $M^+$  220; (iii) 1,5-diphenylpentan-3-imine (4) (61.6%),  $t_R$  6.9 min,  $\delta$  1.3br (s, NH), 1.7 (complex m, 4 H<sub>A</sub>), 2.7 (complex m, 4 H<sub>B</sub>), and 7.15 (m, 10 ArH) (Found: C, 85.7; H, 8.9; N, 5.4. C<sub>17</sub>H<sub>19</sub>N requires C, 86.0; H, 8.1; N, 5.9%;  $m/e$  238, 237 ( $M^+$ ), 220, 175, 131 (PhCH<sub>2</sub>·CH<sub>2</sub>·CN?), 117 (PhCH<sub>2</sub>·CH<sub>2</sub>·C<sup>+</sup>), 105 (PhCH<sub>2</sub>·CH<sub>2</sub><sup>+</sup>), and 91 (PhCH<sub>2</sub><sup>+</sup>). In a repetition, the crude product was stirred with hexane; some toluene-*p*-sulphonamide (0.1 g) was precipitated, filtered off, and dried (m.p. 137 °C).

(b) Experiment (a) was repeated in diethyl ether at 35 °C for 44 h; g.l.c. of the product on column (B) at 230 °C disclosed the same three products: (i) 7.5%, (ii) 18.2%, (iii) 67.9%.

3(5)-Phenyl-5(3)-styrylpyrazole (9).—(a) The sulphonylhydrazone (8 g) and powdered sodium methoxide (3.24 g), dissolved in methanol (100 ml), were heated at 180 °C and 580 lb in<sup>-2</sup> for 2 h. When cool, the solution was poured into water, and the product extracted with ether and dried azeotropically with benzene to give a solid (3 g), m.p. 154–160 °C; crystallisation from chloroform afforded 3(5)-phenyl-5(3)-styrylpyrazole, m.p. and mixed m.p. 162.5 °C (lit.<sup>6</sup> 157–159 °C);  $\delta$  6.67 (s, H<sub>C</sub>), 6.98 (d, H<sub>A</sub> and H<sub>B</sub>), 7.25 (complex m,  $\beta$ -Ph and *m*- and *p*-H of 3-Ph), 7.69 (complex m, two *o*-H of 3-Ph), and 10.2br (s, NH);  $m/e$  247, 246, 245, 218, 217, 215, 142, 141, 116, 115, 104, 91, and 77 (Found: C, 82.65; H, 5.7; N, 11.9%;  $M^+$ , 246.1143. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>: C, 82.9; H, 5.7; N, 11.4%;  $M$ , 246.1157). Hydrogenation over palladium-charcoal in methanol gave 3(5)-phenethyl-5(3)-phenylpyrazole (10),  $\delta$  2.92

(s, 2 H<sub>A</sub> and 2 H<sub>B</sub>), 6.32 (s, H<sub>C</sub>), 7.21 (complex m,  $\beta$ -Ph and *m*- and *p*-H of the 3-Ph), 7.68 (m, two *o*-H of 3-Ph), and 9.15 (s, NH);  $m/e$  249, 248, 238, 167, 157, 149, 133, 131, 128, 105, 104, 91 (base peak), and 77 (Found:  $M^+$ , 248.1309. C<sub>17</sub>H<sub>16</sub>N<sub>2</sub> requires  $M$ , 248.1313).

(b) The sulphonylhydrazone (4 g) and solid sodium methoxide (1.6 g) in bis-(2-methoxyethyl) ether (50 ml) were refluxed for 2 h; work-up gave the pyrazole (2.9 g), m.p. and mixed m.p. 162 °C (from chloroform).

(c) A stirred solution of the sulphonylhydrazone (7 g) and powdered sodium methoxide (3.2 g) in methanol (350 ml) was irradiated with a Hanovia 6515-34 immersion lamp [Corex filter (Hanovia 9700)] for 24 h. The <sup>1</sup>H n.m.r. spectrum of the yellow semi-solid product (5 g), isolated in the usual way, showed it to be mainly the pyrazole; crystallisation from ethanol gave the pyrazole, m.p. 162.5 °C, mixed m.p. 162 °C.

*trans,trans-1,5-Diphenylpenta-1,4-dien-3-ol* (11; R = H).—*trans,trans*-Dibenzylideneacetone (10 g) was reduced with sodium borohydride in methanol to give the alcohol (11; R = H) (8.5 g), m.p. 70–71 °C (lit.<sup>9</sup> 66–68 °C);  $\delta$  2.02 (d, OH), 4.96 (m, H<sub>C</sub>), 6.28 (q, 2H<sub>B</sub>), 6.67 (d, 2H<sub>A</sub>), 7.23 (m, 10 ArH) ( $J_{AB}$  16,  $J_{BC}$  6,  $J_{CD}$  3 Hz; irradiation of the hydroxylic proton signal changed the H<sub>C</sub> signal to a triplet; irradiation of the H<sub>C</sub> signal converted the H<sub>B</sub> signal into a doublet and the hydroxylic proton signal to a singlet; addition of deuterium oxide caused the hydroxylic proton signal to disappear and altered the H<sub>C</sub> signal to a triplet).

*trans,trans-3-Methoxy-1,5-diphenylpenta-1,4-diene* (11; R = Me).—The alcohol (11; R = H) (3.75 g), freshly prepared silver oxide (13 g), potassium hydroxide (0.1 g), and methyl iodide (52 ml) were refluxed for 6 h. Filtration and the usual work-up gave the *methyl ether* (3.3 g), m.p. 52 °C (from ethanol);  $\delta$  3.41 (s, OCH<sub>3</sub>), 4.41 (t, H<sub>C</sub>), 6.20 (q, 2 H<sub>B</sub>), 6.65 (d, 2 H<sub>A</sub>), and 7.33 (m, 10 ArH);  $m/e$  251, 250 ( $M^+$ ), 249, 220, 219 ( $M$  - OMe), 218 [ $\dot{C}(\text{CH}=\text{CHPh})_2$ ], 217, 215, 205–202, 159 ( $M$  - CHPh - H), 147 ( $M$  - CH=CHPh), 144, 141, 131 (<sup>+</sup>O=C·CH=CHPh), 117–115, 105, 103 (<sup>+</sup>CH=CHPh), 91 (base peak), and 77 (Found:  $M^+$ , 250.1355. C<sub>18</sub>H<sub>18</sub>O requires  $M$ , 250.1357). The methyl ether (1 g) was stirred with sodium-potassium alloy (78% K; MSA Research Corp.) in tetrahydrofuran (7 ml) under nitrogen at 0 °C, reacting rapidly to give an intense violet colouration, which changed to deep blue. After 30 min methanol (3 ml) was added followed by water. The product was extracted with ether, and dried azeotropically with benzene to give an oil (0.74 g), which [by g.l.c. on column (A)] contained a single component. Preparative g.l.c. on column (B) at 246 °C gave *cis*- or *trans*-1,5-diphenylpent-2-ene (13),  $\delta$  2.5 (complex m, 2 H<sub>D</sub> and 2 H<sub>E</sub>), 3.32 (d, 2 H<sub>A</sub>), 5.56 (quint, H<sub>B</sub> and H<sub>C</sub>), and 7.23 (m, 10 ArH) (irradiation of the quintet caused the doublet to collapse to a singlet; irradiation of the doublet changed the quintet to a partially resolved multiplet) (Found:  $M^+$ , 222.1414. C<sub>17</sub>H<sub>18</sub> requires  $M$ , 222.1408).

We thank Professor N. S. Bhacca, Louisiana State University, for interpretation of the <sup>1</sup>H n.m.r. spectrum of compound (13). One of us (G. N. H.) acknowledges the tenure of a Welch Post-doctoral Research Fellowship during 1975 and the other (C. W. S.) acknowledges the support of the Robert A. Welch Foundation, Houston, Texas, U.S.A.

\* The centre of the doublet coincides with the centre of the triplet.