Electrocyclic Reactions. Part VIII.[1] Some Reactions of *trans,trans*- and *cis,trans*-2-Bromo-1,5-diphenylpenta-1,4-dien-3-one (α-Bromodibenzylideneacetone)

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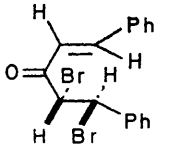
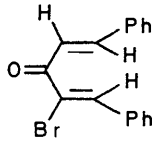
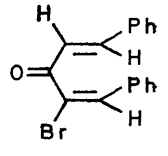
Treatment of *trans,trans*-2-bromo-1.5-diphenylpenta-1,4-dien-3-one and its *cis,trans*-isomer with hot 10% hydriodic acid–acetic acid gave (by reduction) 1.5-diphenylpentan-3-one and (by cyclisation) *trans*-3.4-diphenylcyclopentanone: since the *cis,trans*-isomer rearranges to the *trans,trans*-isomer in the presence of a trace of iodine in refluxing carbon tetrachloride. such rearrangement evidently occurs prior to cyclisation. The *trans,trans*-isomer was little changed by concentrated sulphuric acid at 0 °C. but at 25 °C gave 2-bromo-3,4-diphenylcyclopent-2-enone (40%). *trans*-2-bromo-3.4-diphenylcyclopent-4-enone (18%), and 5-hydroxy-2,3-diphenylcyclopent-2-enone [Vorlander's ketol] (1%). The *cis,trans*-isomer reacted readily with concentrated sulphuric acid at 0 °C to give the above-mentioned three compounds in different proportions (23, 13, and 2%). together with the known dimer of 3.4-diphenylcyclopenta-2.4-dienone (8%), and *cis*-2-bromo-3,4-diphenylcyclopent-4-enone (38%). The formation of these products is discussed in terms of thermal symmetry-allowed conrotatory [$_{\pi}2_{s} + _{\pi}2_{s}$] electrocyclic reactions of the appropriate cations.

trans,trans-DIBENZYLIDENEACETONE on treatment with an equimolar amount of bromine gave in high yield (91%) the dibromide [2] (I). Base-catalysed dehydrobromination of (I) with potassium acetate in refluxing acetic acid gave *trans,trans*-2-bromo-1,5-diphenylpenta-1,4-dien-3-one [3] (II), $\lambda_{max.}$ 324 nm (log ε 4.44), whereas treatment with potassium acetate in dimethylformamide [4] at 20 °C gave a mixture (35 : 65) of (II) and the *cis,trans*-isomer (III), $\lambda_{max.}$ 307 nm (log ε 4.32); samples of (III) of 94% purity could be obtained by column chromatography on aluminium oxide impregnated with silver nitrate, but further purification could not be effected.

The *cis,trans*-isomer (III) readily rearranged to the *trans,trans*-isomer (II) with a catalytic amount of iodine in refluxing carbon tetrachloride. Such rearrangement evidently occurs prior to cyclisation in the reaction with hydriodic acid now to be described.


(I)

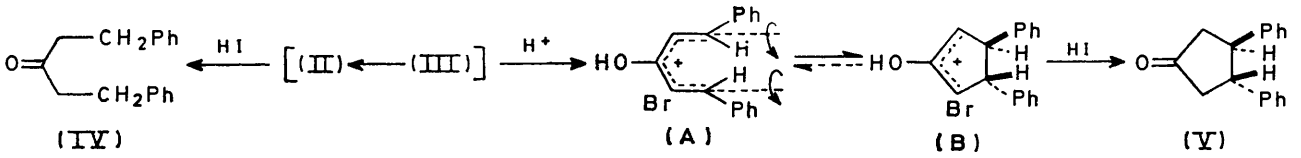

(II)


(III)

Treatment of the *trans,trans*-isomer (II) with 10% hydriodic acid in refluxing acetic acid containing a little

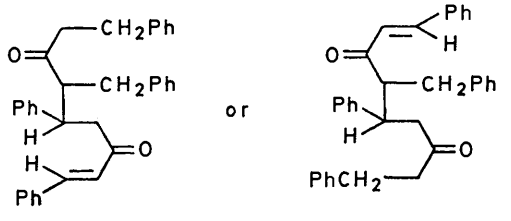
[1] Part VII, C. W. Shoppee and Y-S. Wang, *J.C.S. Perkin I*, 1975, 1595.
[2] P. Groebel, *Ber.*, 1903, **36**, 1498.
[3] G. Hellthaler, *Annalen*, 1914, **406**, 161.
[4] A. Hassner, G. L'Abbe and M. J. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 981.

red phosphorus gave, by reduction, 1,5-diphenylpentan-3-one [5,6] (IV) (20%), and, by cyclisation, *trans*-3,4-diphenylcyclopentanone [6-9] (V) (57%) with involatile polymeric material (8%). The *cis,trans*-isomer (III) furnished the same products in different proportions (10 and 52% respectively), but failed to give *cis*-3,4-diphenylcyclopentanone,[6,7] the expected cyclic product. The results are best explained in terms of a thermal symmetry-allowed conrotatory $[_\pi 2_s + _\pi 2_a]$ electrocyclic reaction, (A) ⟶ (B), and reduction of the single bromine atom, following rearrangement of the *cis,trans*-isomer (III) to the *trans,trans*-isomer (II) (Scheme 1).



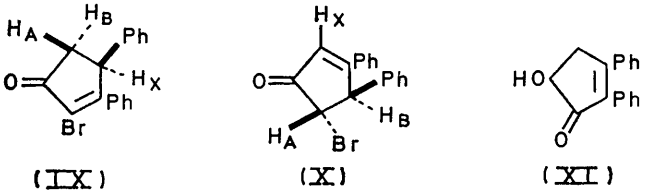
SCHEME 1

Comparison with our earlier results on dibenzylideneacetone [8] and its αα′-dibromo-derivative [9] (VI) is instructive. In the former case, a dimer, tentatively assigned structure (VII) was obtained as the major product, along with small amounts of the *trans*-ketone (V). In the latter case, a 51 : 49 mixture of the ketone (V) and 3,4-diphenylcyclopent-2-enone [10] (VIII) was observed, with the unsaturated ketone resulting from a formal elimination of a benzyl proton from the cyclised dibromo-cation analogous to (B), followed by reduction of the bromo-substituents. In neither case was the reduced ketone (IV) observed. These results can be explained on steric grounds. In the case of dibenzylideneacetone,[8] the least hindered molecule, dimerisation is the predominant pathway, with cyclisation followed by reduction to form



(V) competing to a limited extent. In the case of the αα′-dibromo derivative [9] (VI), the most hindered molecule, dimerisation does not occur, and cyclisation becomes the exclusive mode of reaction. The cyclic dibromo-cation analogous to (B) is, however, sufficiently hindered towards reduction that the formal elimination, giving the unsaturated ketone (VIII), becomes competitive with production of the *trans*-ketone (V). The *trans,trans*-isomer (II) is an intermediate case; the molecule is sufficiently hindered to preclude dimerisation, but not reduction by hydriodic acid to form the saturated ketone (IV). Also, the cation (B) is not hindered towards reduction to the saturated ketone (V), and products from the eliminative pathway are not observed.

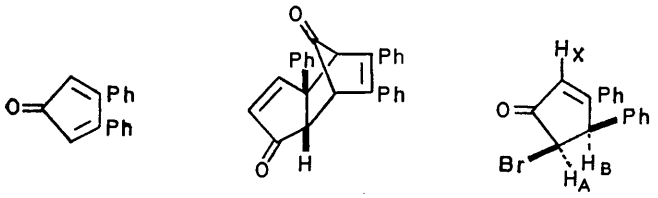
The sulphuric-acid-catalysed cyclisations of the isomers (II) and (III) serve to delineate the eliminative pathway. The *trans,trans*-isomer (II) was little changed by concentrated sulphuric acid at 0 °C, but at 25 °C the resulting red solution, when poured into ice–water, gave 2-bromo-3,4-diphenylcyclopent-2-enone (IX), $\nu_{max.}$ 1 707 cm^{-1}, $\lambda_{max.}$ 284 nm (log ε 4.2), M^+ 312 and 314, showing an ABX pattern in the ^{1}H n.m.r. spectrum (40%); the isomeric *trans*-2-bromo-3,4-diphenylcyclopent-4-enone (X), $\nu_{max.}$ 1 707 and 1 698 cm^{-1}, $\lambda_{max.}$ 291 nm (log ε 4.3—4.4), M^+ 312 and 314 (18%); Vorlander's ketol [8] (XI) (1%); and red polymeric material.



A 65% pure sample of the *cis,trans*-isomer (III) with concentrated sulphuric acid at 0 °C reacted readily to give the three compounds (IX)—(XI), but in different proportions (39, 33, and 3% respectively), together with 3,4-diphenylcyclopenta-2,4-dienone (XII) as the known [11,12] dimer (XIII) (22%), m.p. 209°, $\nu_{max.}$ 1 785 and 1 695 cm^{-1}, M^+ 464 and consistent fragmentation pattern. It has been shown that the dimer (XIII) is not formed from the bromo-ketones (IX) and (X) under the conditions of the reaction or work-up. Use of a 92% pure sample of the *cis,trans*-isomer (III) gave the unchanged *trans,trans*-isomer (II) (6% of the 8% present in the starting material), the three compounds (IX)—(XI) (23, 13, and 2% respectively), the dimer (XIII)

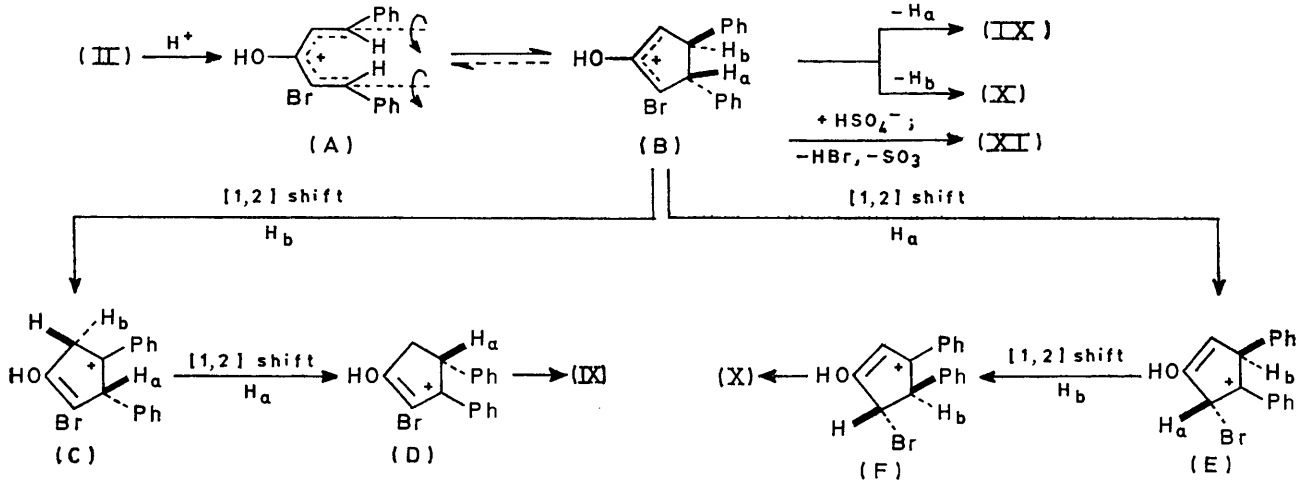
[5] H. O. House, M. Gall, and H. Olmstead, *J. Org. Chem.*, 1971, **36**, 2361.
[6] H. A. Weidlich, *Ber.*, 1938, **71**, 1601; H. A. Weidlich and M. Meyer-Delius, *ibid.*, 1941, **74**, 1195.
[7] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1939, 567.
[8] C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1972, 2271.
[9] C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1973, 2197.
[10] P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Amer. Chem. Soc.*, 1958, **80**, 202.
[11] P. Bladon, S. McVey, P. L. Paulson, G. D. Broadhead, and W. M. Horspool, *J. Chem. Soc.* (*C*), 1966, 306.
[12] B. Fuchs, *J. Amer. Chem. Soc.*, 1971, **93**, 2544.

(8%), and the labile *cis*-2-bromo-3,4-diphenylcyclopent-4-enone (XIV) (38%), $\nu_{max.}$ 1 710 and 1 693 cm^{-1}, as the major product. The structure (XIV) is consistent with the ^1H n.m.r. spectrum; the chemical shift of vinyl proton H_X of (XIV) (δ 6.98) is closely similar to that of the vinyl proton H_X of the stereoisomer (X) (δ 6.91), and the major coupling constant, J_{AB} 7.3 Hz, indicates, as required by formula (XIV), a torsion angle $\theta(H_A/H_B)$ of *ca.* 0°. The structure (XIV) is also supported by the behaviour upon treatment with cold dilute base; the



(XII) (XIII) (XIV)

secondary bromide (XIV) was consumed (63%) to give, by enolisation and inversion of configuration, the stereoisomer (X) (67%), and, by *trans*-dehydrobromination, thermal symmetry-allowed conrotatory $[_\pi 2_s + {}_\pi 2_a]$ electrocyclic reaction (G) ⟶ (H). The cation (H) can again lose a benzylic proton in two ways to furnish, after ketonisation, the bromo-ketones (IX) and (X), or combine with the hydrogen sulphate anion eventually to give Vorlander's ketol (XI), but can also undergo a sequence of suprafacial [1,2] sigmatropic shifts, which relieve the strain caused by the eclipsed phenyl groups, to afford the cations (J) and (K) or (L) and (M). The cation (K), by deprotonation, can give *cis*-2-bromo-3,4-diphenylcyclopent-4-enone (XIV), *trans*-dehydrobrominated to yield the dienone (XII) leading to the dimer (XIII); the cation (M) by deprotonation can give only the bromo-ketone (IX) (Scheme 3). The yields for the bromo-ketones (X) and (XIV) and the dimer (XIII) show that both modes of reaction for apparent elimination of H_b occur, but not to comparable extents; if we assume that treatment of (XIV) with aqueous base forms mixtures (67 : 73) of (X) and (XIII), then 8% of the observed 13% yield of (X) is derived from (XIV) during work-up. Comparison of the yield (5%) of (X) not formed from (XIV) with the total yield (38%) of (XIV) and its



SCHEME 2

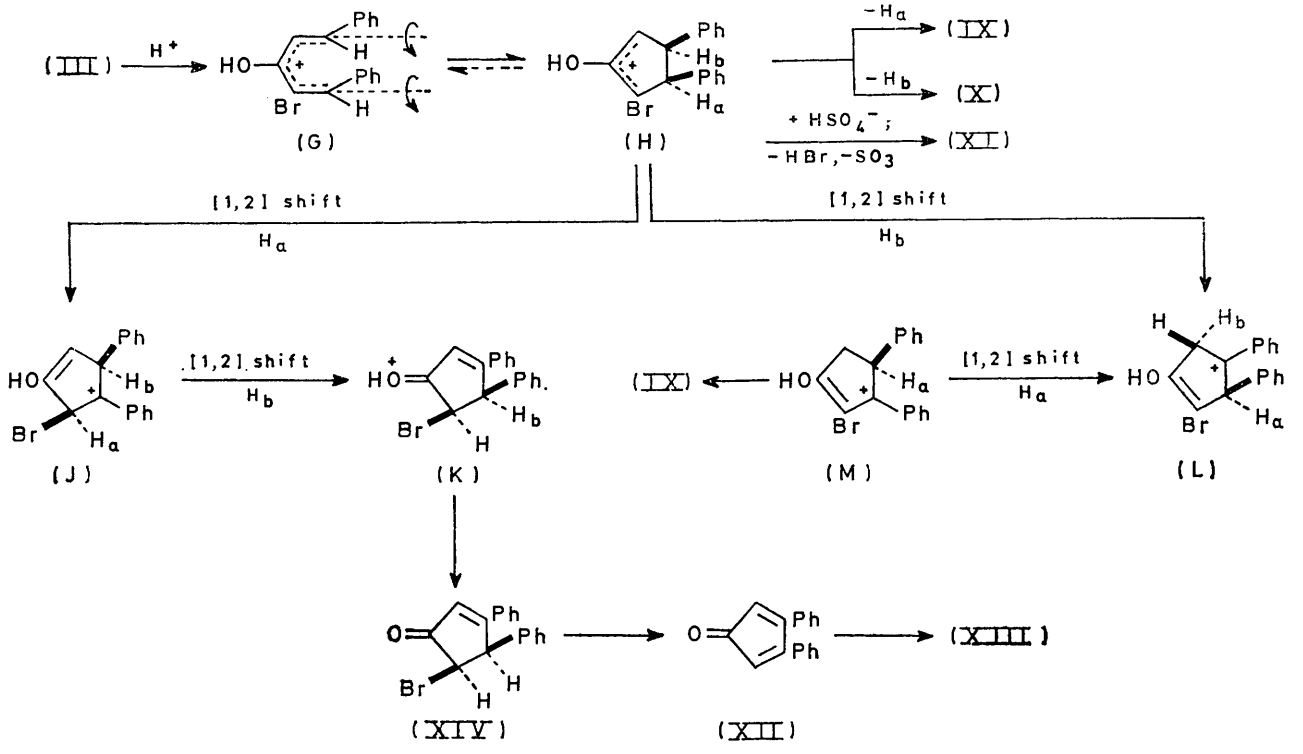
the dienone (XII) as the dimer (XIII) (33%), in a total yield of 68%.

A reaction pathway for the *trans,trans*-bromide (II), leading to the bromo-ketones (IX) and (X), appears to involve a thermal symmetry-allowed conrotatory $[_\pi 2_s + {}_\pi 2_a]$ electrocyclic reaction, (A) ⟶ (B). The cation (B) can lose a benzylic proton to yield, after ketonisation, either (IX) or (X), or combine with the hydrogen sulphate anion to give by concerted loss of hydrogen bromide and sulphur trioxide, followed by prototropy, Vorlander's ketol (XI), but can also undergo a sequence of two suprafacial [1,2] sigmatropic shifts to afford the cations (C) and (D) or (E) and (F) which lead to (IX) and (X), respectively (Scheme 2).

A reaction pathway for the *cis,trans*-bromide (II) must account not only for the formation of the bromo-ketones (IX) and (X) but also for the production of the isomeric bromo-ketone (XIV). A possible pathway involves a transformation products (X) (8%) and the dimer (XIII) (8%) shows that the sequential sigmatropic shift pathway accounts for >90% of the products, and the elimination pathway for <10% of the products. In the case of cation (B) (Scheme 2), however, both modes of reaction give the bromo-ketones (IX) and (X) and distinction between the two pathways cannot be made in the absence of data from suitably labelled substrates.

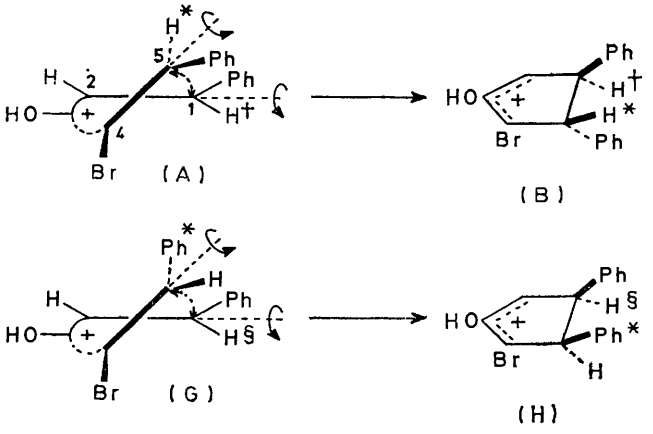
There seems to be no obvious reason for the lesser ease of cyclisation of the *trans,trans*-bromide (II) than of the *cis,trans*-isomer (III) with concentrated sulphuric acid. Inspection of the geometry of the idealised transition states for the conrotatory $[_\pi 2_s + {}_\pi 2_a]$ electrocyclic reaction (II) ⟶ (A) ⟶ (B) (Scheme 2) suggests that the large phenyl groups and the bromine atom are well separated; reversal of geometry at C-5, as in the reaction (III) ⟶ (G) ⟶ (H) (Scheme 3), appears to bring the phenyl groups closer together since the original

ethylenic components must approach one another orthogonally.[13] However, as pointed out by Professor R. Hoffmann (letter of 12 September, 1973): ' There is nothing sacred about absolute orthogonality in the $[2_s + 2_a]$ transition state; as reaction proceeds the components become more and more tilted with respect to each other, and the initial geometry probably approximates to a 45° approach rather than a 90° approach.' A twist angle of 42° has recently been suggested.[14]



SCHEME 3

The repulsions H*/H‡ in the transition state (A) and Ph*/H§ in the transition state (G) are minimised by



conrotation as the reaction co-ordinates are traversed to give (B) and (H), respectively. If it is assumed that the unknown transition state energies of (A) and (G) are approximately equal, since the ground state energy for the *trans,trans*-bromide (II) is clearly less than that for the *cis,trans*-bromide (III), then the activation energies for the cyclisation will be $\Delta G^{\ddagger}_{cis,trans} < \Delta G^{\ddagger}_{trans,trans}$ in accord with the results reported above.

* Solutions in chloroform give carbonyl bands *ca.* 15 cm^{-1} lower than those observed in carbon tetrachloride.[15]

EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Thomas 40 hot-stage apparatus. U.v. spectra (ethanolic solutions) were measured with a Beckman Acta III spectrometer; i.r. spectra (solutions in chloroform * unless otherwise specified) were measured with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were recorded with Varian A60 and XL100 instruments for solutions in deuteriochloroform unless otherwise specified, 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) or silica gel (Davidson). T.l.c. was carried out using silica gel G or F (Merck); plates prepared with silica gel G were developed by exposure to iodine vapour; plates made with silica gel F were examined in u.v. light. G.l.c. was carried out with a Beckman GC45 chromatograph fitted with a flame ionisation detector and a 6 ft × ⅛ in column packed with 5% XE60 (helium flow rate 40 ml min^{-1}; temperature programming from 100 to 200° during 8 min).

erythro-1,2-*Dibromo*-1,5-*diphenylpent*-4-*en*-3-*one* (trans,

[13] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 69.

[14] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 6809.

[15] A. R. H. Cole, *Rev. Pure Appl. Chem.*, 1954, 4, 1190.

trans-*Dibenzylideneacetone Dibromide*) (I).—Addition of an equimolar amount of bromine to *trans,trans*-dibenzylideneacetone in carbon tetrachloride at 25 °C gave the *erythro*-dibromide (91%), m.p. 172—174° (from ether–heptane) [lit.,[2] 163° (decomp.)], $\nu_{max.}$ 1 685, 1 660, and 1 602 cm^{-1}, δ 5.27 and 5.60 [2 H, q, AB pattern (J 11 Hz)], 7.02 and 7.97 [q, 2 vinyl H, AB pattern (J 16 Hz)], and 7.5br (10ArH, m), M^+ 396/394/392 (1 : 2 : 1), *m/e* 315/313 (M − Br), 234 (M − Br_2), 205, 131 ($PhCH{=}CHCO^+$), 103 ($PhCH{=}CH^+$), and 77 (Ph^+) (Found: M^+, 393.9388. Calc. for $C_{17}H_{14}Br^{79}Br^{81}O$: M, 393.9380).

trans,trans-2-*Bromo*-1,5-*diphenylpenta*-1,4-*dien*-3-*one* (II).—The *erythro*-dibromide (I) (4 g) was dissolved in 0.62N-potassium acetate in acetic acid (150 ml; prepared from potassium carbonate and acetic acid). The clear solution was refluxed for 1.5 h and poured into 2N-K_2CO_3; the suspension was stirred for 45 min, and the solid filtered off, washed with water, and dried in a vacuum (3.1 g). Recrystallisation from n-heptane gave *trans,trans*-2-bromo-1,5-diphenylpenta-1,4-dien-3-one, m.p. 61—63° (lit.,[3] 66°), $\lambda_{max.}$ 324 nm (log ε 4.44), $\nu_{max.}$ 1 665, 1 610, and 1 577 cm^{-1}, δ 7.2—7.7 (m, 8ArH), 7.57 and 7.91 (AB pattern, J 15.5 Hz, 2 vinyl H), 7.85—8.0 (m, 2 *o*-H from 1-phenyl), and 8.18 (s, 1 vinyl H), *m/e* 233 (M − Br, base peak), 131 ($PhCH{=}CHCO^+$), and 103 ($PhCH{=}CH^+$) (Found: C, 65.8, 65.9; H, 4.5, 4.5; Br, 24.3, 24.1%; M^+, 312.0138. Calc. for $C_{17}H_{13}BrO$: C, 65.2; H, 4.2; Br, 25.5%; for $C_{17}H_{13}Br^{79}O$: M^+, 312.0139).

cis,trans-2-*Bromo*-1,5-*diphenylpenta*-1,4-*dien*-3-*one* (III).—The *erythro*-dibromide (I) (3.65 g) in 0.26N-sodium acetate was dissolved in dimethylformamide (175 ml); the solution was stirred at 25 °C for 1.5 h, and poured into distilled water (1.5 l). The product was extracted with ether (3 × 150 ml); the extract was washed with water (2 × 500 ml), dried with potassium carbonate, and evaporated in a vacuum. The resultant oil (2.64 g) was shown by u.v. analysis to contain 35% of the *trans,trans*-isomer (II). A 63% pure sample (5 g) of the *cis,trans*-compound (III) was placed on a 5% silver nitrate–neutral aluminium oxide column; elution with ether–hexane (3 : 7) gave 60—70% pure (III) (0.55 g) and 94% pure (III) (2.36 g). Continued elution with ether–hexane mixtures, followed by benzene, yielded (II) of *ca.* 90% purity (1.48 g). Attempts further to purify samples of (III) by recrystallisation from hydrocarbon solvents afforded only oils. Further column chromatography and high-pressure liquid chromatography failed to effect further purification of *cis,trans*-2-bromo-1,5-diphenylpenta-1,4-dien-3-one (III), which had $\lambda_{max.}$ 307 nm (log ε 4.32), $\nu_{max.}$ 1 645 and 1 608 cm^{-1}, δ 6.72 and 8.70 [2 vinyl H, AB pattern (J 16 Hz)], 7.30 and 7.38 (m, 10ArH), and 7.46 (s, 1 vinyl H). Refluxing (III) (177 mg) with a trace of iodine (2 mg) in carbon tetrachloride (15 ml) for 18 h, and the usual work-up, gave material (171 mg), whose i.r. spectrum was identical with that of (II); crystallisation from aqueous methanol gave the *trans,trans*-bromo-ketone (II), m.p. 63—65°.

Cyclisations with Hydriodic Acid–Acetic Acid.—(*a*) The *trans,trans*-bromo-ketone (II) (500 mg) and red phosphorus (500 mg) in a 10% solution of (48%) hydriodic acid in acetic acid (30 ml) were refluxed for 18 h; the cooled mixture was filtered into saturated potassium carbonate solution (600 ml). The precipitate was filtered off and washed with ether, and the filtrate extracted with ether; the combined ethereal solutions were washed with 10% sodium thiosulphate solution and water, dried, and evaporated. The product (315 mg), $\nu_{max.}$ 3 060, 1 735, 1 708, and 1 600 cm^{-1}, after removal of a sample for g.l.c. analysis, was triturated with heptane to give, by filtration, *trans*-3,4-diphenylcyclopentanone (V), m.p. 176—178° (lit.,[7] 177°), characterised as the 2,4-dinitrophenylhydrazone, m.p. 169—171° (lit.,[7] 170°). Evaporation of the heptane filtrate gave 1,5-diphenylpentan-3-one (IV) as an oil, $\nu_{max.}$ 1 710 cm^{-1}, δ 2.75 (A_2B_2 pattern of eight broad lines with pairs symmetrically displaced from the centre by 2, 7, 14, and 18 Hz) and 7.27 (m, 10ArH). G.l.c. analysis on a 5% XE60 column gave (IV) (20%; t_R 9.1 min) and (V) (57%; t_R 9.8 min; identical with that of a genuine specimen); part of the sample (8%) was involatile and remains uncharacterised.

(*b*) The *cis,trans*-bromo-ketone [(III); containing 35% of the *trans,trans*-isomer (II)] (540 mg) was treated as under (*a*). The precipitate (163 mg) had m.p. 130—174°, $\nu_{max.}$ 3 060, 1 738, 1 710, and 1 600 cm^{-1}; extraction of the filtrate with ether gave semisolid material (93 mg). G.l.c. analysis of both fractions and combination gave (IV) (8%; t_R 9.1 min), (V) (52%; t_R 9.8 min), and involatile material (6%). The precipitate (148 mg) [containing by g.l.c. analysis 112 mg of (V)] by recrystallisation from chloroform–heptane (3 : 7) furnished (V) (100 mg), m.p. 176°.

Cyclisations with Concentrated Sulphuric Acid.—(*a*) The *trans,trans*-bromo-ketone (II) (230 mg) was dissolved in concentrated sulphuric acid (20 ml); the red solution was stirred at 25 °C for 2.5 h and poured onto ice. The product was extracted with ether (3 × 75 ml); the extract was washed with 2N-sodium hydroxide and with water, dried, and evaporated in a vacuum. The product (143 mg) had $\nu_{max.}$ 1 708, 1 595, 1 568, and 665 cm^{-1}; the ^1H n.m.r. spectrum showed the presence of starting material (II) (4%) and of a 69 : 31 mixture (58%) of (IX) and (X). These major components were separated by column chromatography (silica gel; 5—20% diethyl ether in hexane) and recrystallisation to afford 2-*bromo*-3,4-*diphenylcyclopent*-4-*enone* (X), m.p. 108—110°, $\nu_{max.}$ 3 080, 1 710, 1 600, and 1 573 cm^{-1}, δ 4.32 (d, H_A, J_{AB} 2 Hz), 5.92 (t, H_B, $J_{AB} \simeq J_{BX}$ 1.5—2 Hz), 6.91 (d, H_X, J_{BX} 1.5 Hz), and 7.0—8.0 (m, 10ArH); M^+ 314/312, *m/e* 233 (M − Br, base peak), 205, 204, 202, 102, 101 ($PhC{\equiv}C^+$), and 91 ($PhCH_2^+$) (Found: C, 65.2; H, 4.2; Br, 25.2%; M^+, 312.0144. $C_{17}H_{13}Br^{79}O$ requires C, 65.2; H, 4.2; Br, 25.5%; M, 312.0139) and an 80% pure (by ^1H n.m.r. analysis) sample of 2-bromo-3,4-diphenylcyclopent-2-enone (IX), m.p. 123—126°, characterised as described below. Acidification of alkaline washings gave a precipitate (2 mg), whose i.r. spectrum was identical with that [8] of Vorlander's ketol (XI).

(*b*) The *cis,trans*-bromoketone [(III); containing 35% of the *trans,trans*-isomer (II)] (1.9 g) was dissolved in ice-cold concentrated sulphuric acid (30 ml); the red solution was stirred while warming to room temperature for 1.5 h, and then worked up as in (*a*). The neutral product (1.78 g) was shown by ^1H n.m.r. analysis to consist of a 39 : 33 : 22 mixture of (IX), (X), and (XIII). Fractional crystallisation from aqueous methanol afforded little resolution of the mixture, but one fraction, m.p. 110—125° (0.79 g), on recrystallisation from heptane and separation by hand-picking gave 2-*bromo*-3,4-*diphenylcyclopent*-2-*enone* (IX), m.p. 128—131°, $\nu_{max.}$ 1 707, 1 598, 1 570, and 665 cm^{-1}, δ 2.58, 3.25, and 5.66 (ABX pattern, J_{AB} 19, J_{AX} 2, J_{BX} 7 Hz), and 7.15—7.55 (m, 10ArH), M^+ 314/312 (1 : 1), *m/e* 233 (M − Br), 205, 129 ($PhC{\equiv}C{-}CO^+$), 105, 104, 103 ($PhCH{=}CH^+$), 102, 101 ($PhC{\equiv}C^+$), 91 ($PhCH_2^+$), and 77 (Ph^+) (Found: C, 66.2, 66.2; H, 4.4, 4.5; Br, 25.4, 25.3%;

M^+, 312.0138. $C_{17}H_{13}Br^{79}O$ requires C, 65.2; H, 4.2; Br, 25.5%; M^+, 312.0139). Column chromatography of the residual material on neutral alumina failed to yield (IX) and (X), which probably decomposed on the column, but elution with ether–hexane (3 : 7) gave a red oil (80 mg), $\nu_{max.}$ 1 725 cm^{-1}, and use of ether–hexane (1 : 1) gave the dimer (XIII), m.p. 209—210° (decomp.) [from chloroform–heptane (3 : 7)], $\nu_{max.}$ 1 785 and 1 695 cm^{-1}, δ 3.17 (d, *J* 2 Hz), 3.85 (dd, *J* 4.5 and 2 Hz), and 4.5 (d, *J* 2 Hz) [lit.,[11,12] m.p. 209°, $\nu_{max.}$ (KBr) 1 780 and 1 690 cm^{-1}, δ 3.13 (d, *J* 2 Hz), 3.82 (dd, *J* 5 and 2 Hz), and 4.5 (d, *J* 2 Hz)], M^+ 464, *m/e* 436 (*M* — CO), 408 (*M* — 2 CO), 407, 359 (*M* — CO — Ph), 331 (*M* — CO — Ph — CO), 306, 291, 289, 252, 232 (monomer), 204, 203, 202, and 102 (base peak, $[PhC{\equiv}CH]^+$). The alkaline washings on acidification yielded material (50 mg), m.p. 170° after softening from 160°, whose i.r. spectrum was identical with that [8] of Vorlander's ketol (XI).

(*c*) The *cis,trans*-bromo-ketone [(III); containing 8% of the *trans,trans*-isomer (II)] (600 mg) was treated with concentrated sulphuric acid (10 ml) as in (*b*). After quenching with ice, the product was extracted with ether. The extract was washed with cold 3% sodium carbonate solution, dried ($CaCl_2$), and evaporated in a vacuum to give a yellow oil (520 mg), $\nu_{max.}$ 1 710, 1 595, 1 565, 1 458, and 1 445 cm^{-1}. Acidification of the basic washings, followed by extraction with chloroform, yielded crude Vorlander's ketol (XI) (12 mg). The neutral fraction deposited crystals, which were physically separated (1 mg), and are regarded as *cis*-2-bromo-3,4-diphenylcyclopent-4-enone (XIV), m.p. 92—93°, $\nu_{max.}$ 1 710 and 1 693 cm^{-1}. ^1H N.m.r. analysis of the remainder of the neutral fraction showed it consisted of a mixture of (II) (6%), (IX) (23%), (X) (13%), (XIII) (8%), and (XIV) (38%). Crystallisation of a portion (320 mg) of the neutral fraction from ether–hexane (1 : 9) at −15 °C gave crystals, m.p. 88—96°, $\nu_{max.}$ 1 710, 1 600, 1 490, and 1 446 cm^{-1}, shown by ^1H n.m.r. analysis to consist of a mixture of (IX) and (XIV) in the ratio 30 : 70. Recrystallisation did not alter the physical properties or composition; attempts to purify this material and the residual portion of the neutral fraction by preparative t.l.c. on silica plates with ether–hexane (3 : 7) failed. Preparative t.l.c. similarly failed to isolate (XIV) from the neutral fractions of replicate runs, as did attempted fractional crystallisation. Another portion (200 mg) of the neutral fraction, containing (IX) (53 mg), (X) (29 mg), and (XIV) (90 mg) was dissolved in ether (50 ml) and shaken mechanically with N-NaOH at 25 °C for 15 min; the ethereal layer by separation and evaporation in a vacuum yielded a yellow oil (190 mg). ^1H N.m.r. analysis showed a decrease of (XIV) (34 mg), an increase of (X) 41 mg), and an increase of the dimer (XIII) (35 mg); the amount of the vinyl bromide (IX) remained unchanged within *ca.* 5%.

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