# Intramolecular Electrocyclic Reactions. Part II.[1] Reactions of 1,5-Diphenylpenta-1,4-dien-3-one

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An intramolecular electrocyclic reaction of 1,5-diphenylpenta-*trans*-1,*trans*-4-dien-3-one as the cation (generated with acetylium ions) affords, by conrotatory cyclisation, 2-acetoxy-*trans*-4,5-diphenylcyclopent-2-enyl sodium sulphate (XI), which is hydrolysed by hot 2N-sodium hydroxide or sodium carbonate solution with concomitant pinacolic change to 5-hydroxy-2,3-diphenylcyclopent-2-enone (X), sodium acetate, and sodium sulphite. Generation of the same cation with hydriodic acid gives, by conrotatory cyclisation and reduction, *trans*-3,4-diphenylcyclopentanone (VII) in 13% yield.

1,5-DIPHENYLPENTA-1,4-DIEN-3-ONE (dibenzylideneacetone) exists in three geometrically isomeric forms;[2] *trans,trans*, m.p. 111° (I), *cis,trans*, m.p. 60° (II), and *cis,cis*, b.p. 130° at 0·02 mmHg (III). The *cis,cis*-isomer (III) on treatment with mineral acid gives a mixture of the isomers (I) and (II).[2] We have examined some cyclisation reactions of the *trans,trans*-isomer (I) and intend later to investigate those of the *cis,trans*-isomer (II).
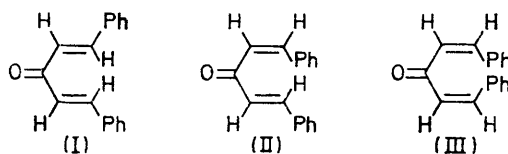
In 1903, Vorlander and Schrödter[3] found that the *trans,trans*-dienone (I) gives salts with conc. sulphuric acid[4] but is otherwise unchanged; we have made similar observations with phosphoric acid (*cf.* ref. 5). The ketone (I) is stable to conc. sulphuric acid and stable to acetic anhydride,[3] but is converted by treatment with conc. sulphuric acid *and* acetic anhydride[3] at 25—30° for some hours into an intermediate hydrogen sulphate, m.p. 109°, giving on mild alkaline

hydrolysis Vorlander's ketol, $C_{17}H_{14}O_2$, m.p. 176°. In 1904, Vorlander and von Liebig[6] showed that oxidation of the ketol with chromium trioxide–acetic acid gives benzil and 3-benzoyl-3-phenylpropionic acid (IV), and reduction with hydriodic acid and phosphorus gives *cis*-1,2-diphenylcyclopentane,[7] (VI). In 1914, von Liebig[8] repeated the work of Vorlander and Schrödter[3] and suggested formula (V) for the ketol.
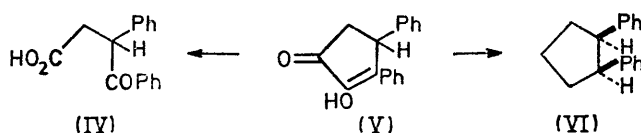
The initial product of the reaction of the ketone (I) with conc. sulphuric acid–acetic anhydride was regarded[3] as an acetylated cyclopentenyl hydrogen sulphate, isolated as the sodium salt,[3] $AcO-C_{17}H_{14}-OSO_3Na$, or the corresponding potassium salt.[3,8,9] The cyclopentane ring structure must be present in the acetylated potassium salt, since Metge[9] by reduction of this, or of the analogous sodium salt, in acetic acid, or of Vorlander's ketol in potassium hydroxide solution, with sodium amalgam obtained *trans*-3,4-diphenylcyclopentanone (VII). Shoppee and Burton[10] repeated the last-named

[1] Part I, C. W. Shoppee and R. E. Lack, *J. Chem. Soc.* (*C*), 1969, 1346.
[2] J. G. Dinwiddie, jun., H. M. White, and W. J. Day, *J. Org. Chem.*, 1962, **27**, 327.
[3] D. Vorlander and G. Schrödter, *Ber.*, 1903, **36**, 1490.
[4] M. J. S. Dewar, *J. Chem. Soc.*, 1946, 406.

[5] H. Stobbe and R. Härtel, *Annalen*, 1909, **370**, 99, esp. 118.
[6] D. Vorlander and H. J. von Liebig, *Ber.*, 1904, **37**, 1133.
[7] H. A. Weidlich, *Ber.*, 1938, **71**, 1601.
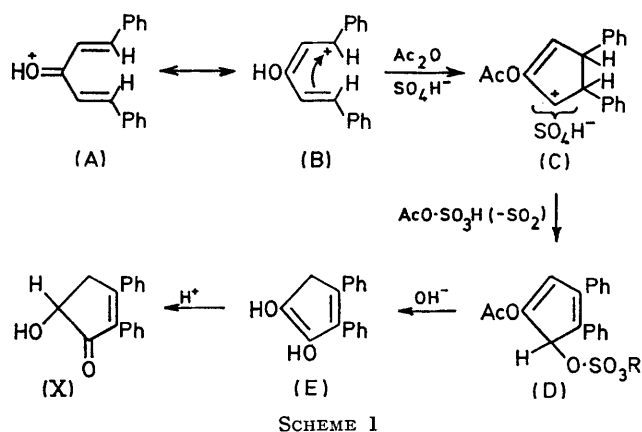[8] H. J. von Liebig, *Annalen*, 1914, **405**, 188, 209.
[9] G. Metge, Dissertation, Hallé, 1904.
[10] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1939, 567.

experiment and isolated the *trans*-ketone [7] (VII) (the product of 1,4-reduction) together with some *cis*-ketone [7] (VIII) (the product of 1,2-reduction) and a 3,4-diphenylcyclopentane-1,2-diol (IX); they characterised both the ketones (VII) and (VIII) by preparation of bis-(3,4-methylenedioxy)benzylidene derivatives and 2,4-dinitrophenylhydrazones.

(VII) (VIII) (IX)
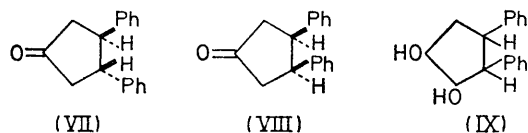
In 1955, Allen *et al.*[11] modified formula (V) for Vorlander's ketol to the structure (X) on account of the u.v. spectrum and the formation of an osazone. We have confirmed formula (X) by the mass spectrum (M^+ 250), the i.r. spectrum ($\nu_{max.}$ 3475 and 1690 cm^{-1}), and the

(A) (B) $\xrightarrow{Ac_2O}{SO_4H^-}$ (C)

$\downarrow AcO \cdot SO_3H \, (-SO_2)$

(X) $\xleftarrow{H^+}$ (E) $\xleftarrow{OH^-}$ (D)

SCHEME 1

n.m.r. spectrum (ABX pattern). Allen *et al.* suggested for the formation of Vorlander's ketol (X) a mechanism which may be represented as in Scheme 1. The mechanism of the oxidation of the cyclopentene (C) to the cyclopentadiene (D) is not discussed in ref. 11.

The product of the cyclisation of the *trans,trans*-dienone (I) with acetic anhydride–sulphuric acid, after quenching with ice-cold potassium carbonate, is the acetoxycyclopentenyl potassium sulphate [as (XI)]. The corresponding sodium salt (XI) was prepared from the potassium salt; the u.v. spectrum (methanol) shows a broad peak at 301 nm (log ε *ca.* 2) corresponding to the carbonyl function in the acetoxy-group, a set of small aromatic absorption bands at 268, 265, 258, 253, and 248 nm (log ε <2·6), but no selective absorption of moderate intensity at 235—240 nm, corresponding to a homoannular diene [cyclopentadiene [12] has $\lambda_{max.}$ 238 nm (log ε 3·6)]. We were unable to obtain the *o*-toluidine salt described in ref. 11. The i.r. spectrum of the sodium salt could only be determined in the solid phase owing to insolubility: $\nu_{max.}$ (KBr) 1765 (C=O), 1720 (C=C), and 1220 (C–OAc) for a vinyl acetate,[13] and 1075 and 1030 cm^{-1} (–SO$_3$Na?).

[11] C. F. H. Allen, J. A. Van Allen, and J. F. Tinker, *J. Org. Chem.*, 1955, **20**, 1387.

The acetoxycyclopentenyl sodium sulphate (XI) was too sparingly soluble in deuterium oxide to give a satisfactory n.m.r. spectrum. However, a solution in dimethyl sulphoxide showed a signal for ten aromatic protons, a singlet for one acetyl group, and signals for four other protons (Table). Irradiation at τ 4·15 (H$_A$) left the quartet at τ 6·1 unchanged, but caused the four-line signals at τ 6·5 and 6·8 to collapse

TABLE

N.m.r. signals of the acetoxycyclopentenyl sodium sulphate (XI) in dimethyl sulphoxide at 35 and 105 °C

(XI)

Proton	Ar	H$_A$	H$_B$	H$_C$	H$_D$	H$_{Ac}$
τ	2·8 (10H, m)	4·15 (1H, q)	6·1 (1H, q)	6·5 (1H, dd)	6·8 (1H, dd)	8·0 (3H, s)
J/Hz		J_{AB} 0	J_{AC} 0·7	J_{AD} 12	J_{BC} 7	J_{BD} 11	J_{CD} 0

to doublets; it appears therefore that H$_A$ is coupled allylicly to H$_C$ (J_{AC} 0·7 Hz) and vicinally to H$_D$ (J_{AD} 12 Hz). We cannot account for the large value of J_{AD} unless interaction between H$_A$ and the charged oxygen atoms of the sulphate group alters the geometry of the molecule. The coupling constants J_{BD} and J_{BC} are consistent with a *trans*-arrangement of H$_B$ and H$_D$, and possibly of H$_B$ and H$_C$.

The mass spectrum of the sodium salt (XI) did not show a molecular ion (M^+ 396) and contained a series of peaks [m/e 466, 465, 464, 436, 292, 250 (base peak), 234, 232, 222, 204, and 178] which varied in relative intensity from run to run, and indicated that the compound is thermally unstable, forming dimeric products. The peak at m/e 292 appears to correspond to loss of sodium

(XI) $\longrightarrow$ 396 $\longrightarrow$ 292

$\downarrow$

42 + 250
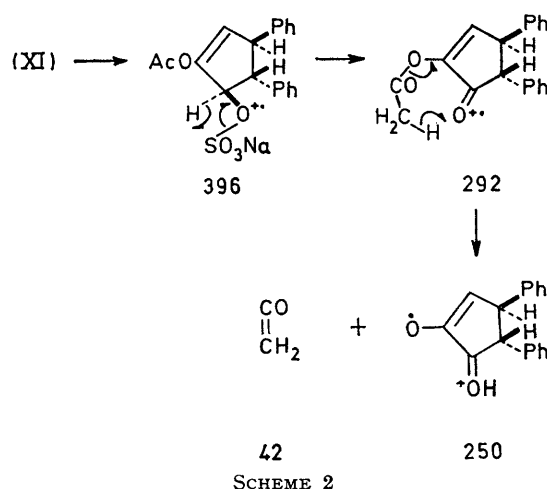
SCHEME 2

hydrogen sulphite (104 m.u.), which suggests a thermal or electron-impact decomposition sequence involving elimination of keten to give the base peak (Scheme 2).

[12] D. Peters, *J. Chem. Soc.*, 1959, 1762.
[13] H. O. House and V. Kramar, *J. Org. Chem.*, 1963, **28**, 3362.

The peak at m/e 178 probably corresponds to diphenyl-acetylene.

Compound (XI) when heated with hydriodic acid and red phosphorus for 8 h gave a product shown to contain four components by g.l.c. These were (i) *cis*-1,2-di-phenylcyclopentane [7] (VI) (0·1%), (ii) *trans*-1,2-diphenyl-cyclopentane [7] (XII) (46%), (iii) an unidentified di-phenylcyclopentene (XIII?) (16%), and (iv) an un-identified diphenylcyclopentenone (XIV?) (29%), of which (i) and (ii) were identified by comparison of retention times with those of authentic samples; (iv) was responsible for a peak at 1690 cm^{-1} in the i.r. spectrum of the crude product, and had the same retention time as a genuine specimen of 3,4-diphenylcyclopent-2-enone [14,15] (XIV), $\nu_{max.}$ 1710 and 1680 cm^{-1}. When the reaction time was extended to 20 h the product pro-portions were (i) 0·05%, (ii) 71%, (iii) 21%, and (iv) 2%; thus the unidentified diphenylcyclopentenone may be a precursor of *trans*-1,2-diphenylcyclopentane. The iso-lation of compound (XII) in 46% yield and the virtual absence of the *cis*-isomer (VI) are consistent with the n.m.r. data for the orientations of H_B and H_D assigned in (XI), and prove that these hydrogen atoms possess the *trans*-configuration.
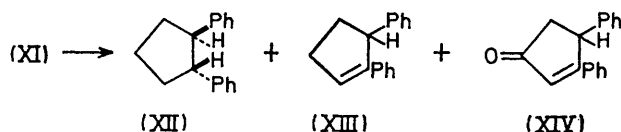
Hydrogenation of the sodium salt (XI) with platinum oxide in methanol, and subsequent alkaline hydrolysis and reduction to eliminate a sulphite group, gave no identifiable product.

Alkaline hydrolysis of the acetoxycyclopentenyl sodium sulphate (XI) by brief boiling with a dilute solution of sodium hydroxide or sodium carbonate gave Vorlander's ketol (X), sodium acetate, and sodium sulphite (*cf.* refs. 3 and 8). The formation of sodium sulphite suggests that the reaction involves a pinacolic rearrangement of the general form: [16]
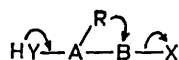

We assume that the enol acetate group of structure (XI) is first rapidly hydrolysed to give by ketonisation the ketonic intermediate (XV), which undergoes a concerted pinacolic process with loss of the sodium sulphite anion to yield the α-hydroxy-$\alpha\beta$-unsaturated ketone (XVI); this by triad prototropy affords the α-ketol (XVII), transformed by further prototropy [17] into Vorlander's ketol (X).

We believe that the conversion of the *trans,trans*-dienone (I) into the acetoxycyclopentenyl sodium sul-phate (XI) involves a thermal intramolecular electro-

cyclic reaction, whose stereochemistry is controlled by conservation of orbital symmetry (Scheme 3). The
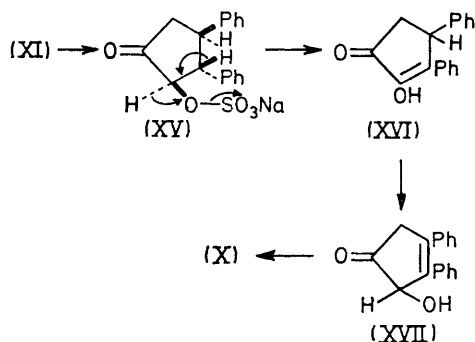
circumstance that both acetic anhydride and conc. sulphuric acid (2 : 3) are necessary (a few drops of conc. sulphuric acid will not do [3]) indicates that the acetylium ion ($Ac_2O + H_2SO_4 \rightleftharpoons Ac^+ + AcOH + HSO_4^-$) is im-plicated in the reaction, and is responsible for its irreversibility. We suggest that the ketone (I) combines with an acetylium ion to give the acetoxycyclopenta-dienyl cation (F), which undergoes conrotatory cyclis-ation in accord with the Woodward–Hoffmann Rules.[18] If 4 π-electrons are involved, (F) by conrotation gives the acetoxy-*trans*-3,4-diphenylcyclopentenyl cation (G); if the oxygen lone pair in the p-orbital parallel to the carbon p-orbitals is implicated, 6 π-electrons are involved but conrotation still gives the cation (G) (see Appendix). The cation (G) reacts with the hydrogen sulphate anion
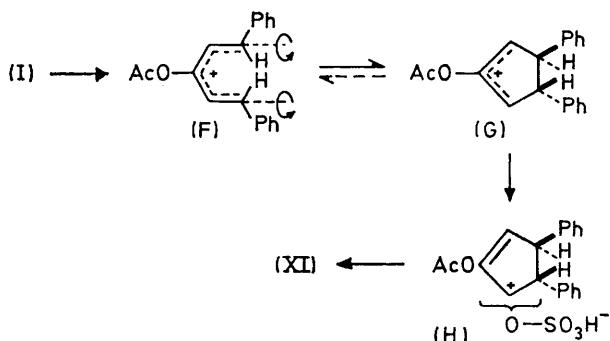
SCHEME 3

to yield the acetoxy-*trans*-3,4-diphenylcyclopentenyl hydrogen sulphate (H), isolated by Vorlander and Schrödter,[3] converted by cold sodium carbonate into the salt (XI).

We have also examined the reaction of the *trans,trans*-dienone (I) with hydriodic acid. This reaction was first carried out in 1904 by Metge,[9] who obtained a small amount of a compound, $C_{17}H_{16}O$, m.p. 172°. We have isolated (by column chromatography followed by g.l.c.) in 13% yield *trans*-3,4-diphenylcyclopentanone [7,10] (VII), m.p. 175°, characterised as its 2,4-dinitrophenyl-hydrazone,[10] and by its mass spectrum; this shows the

[14] F. R. Japp and G. D. Lander, *J. Chem. Soc.*, 1897, **71**, 123.
[15] P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Amer. Chem. Soc.*, 1958, **80**, 202.
[16] C. W. Shoppee, *Proc. Leeds Phil. Soc., Sci. Sect.*, 1928, **1**, 301.
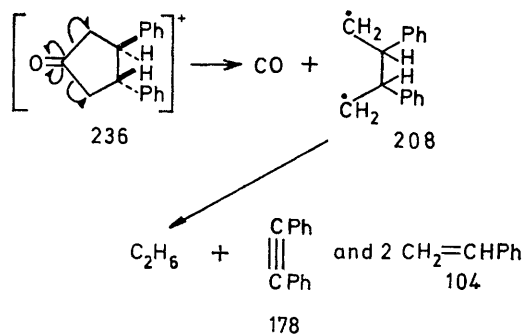
[17] C. W. Shoppee, *J. Chem. Soc.*, 1928, 1662.
[18] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 45.

molecular ion at m/e 236, the base peak at m/e 104, and a fragmentation pattern which may be rationalised as in Scheme 4. The *trans*-ketone (VII) appears to arise by

SCHEME 4

a thermal conrotatory intramolecular electrocyclic reaction of the pentadienyl cation (J) to the cyclopentenyl cation (K) followed by reduction of the derived cyclopentenyl iodide (L).
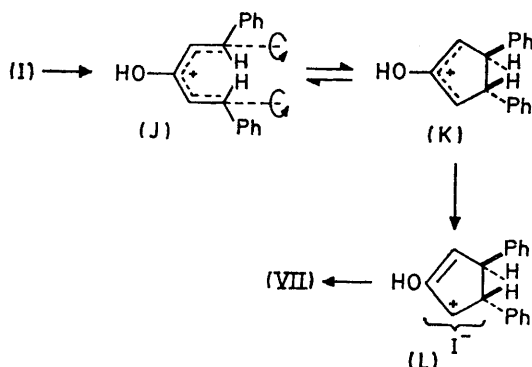
The main product (56%) of the reaction of the ketone (I) with hydriodic acid and phosphorus is a dimeric
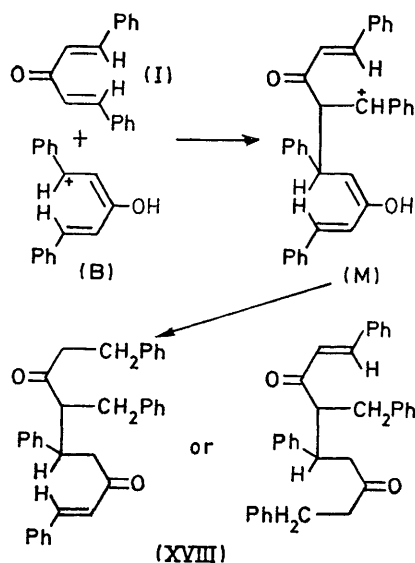
species, $C_{34}H_{32}O_2$ (XVIII), m.p. 185°, $\nu_{max.}$ 1708 (CO), 1670 (C=C–C=O), and 1600 (C=C) cm^{-1}, m/e 472 (M^+) and

381 (base peak, M − PhCH$_2$), giving a yellow 2,4-dinitrophenylhydrazone. It appears to arise by addition to the unprotonated ketone (I) of the protonated form (B), with subsequent reduction of the cationic intermediate (M). Significant amounts (30—40%) of presumably polymeric materials, involatile on g.l.c. and not eluted on column chromatography, are also formed.

EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Köfler hot-stage apparatus, and are corrected. U.v. spectra for solutions in ethanol 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 measured with Varian A60 and XL100 instruments with tetramethylsilane as internal reference. Mass spectra were measured with an A.E.I. MS9 double-focus spectrometer. Column chromatography was performed on aluminium oxide (Woelm, neutral). T.l.c. was carried out on silica gel G or F (Merck); plates prepared with silica gel G were developed by exposure to iodine vapour, and plates made with silica gel F were examined in u.v. light. G.l.c. was carried out either with a Beckman GC45 chromatograph fitted with a flame ionisation detector and a 6 ft × 1/8 in column packed with 5% XE60 (helium flow rate 40 ml min^{-1}, temperature programming 100—200 °C), or for preparative injections, with an Aerograph Autoprep model 700 [columns of Carbowax 20M (for hydrocarbons) or SE30 (for ketones)].

*2-Acetoxy-*trans*-4,5-diphenylcyclopent-2-enyl Potassium and Sodium Sulphates* (XI).—Prepared from the *trans,trans*-dienone (I) (5 g) by the procedures described by Vorlander and Schrödter [3] as modified by von Liebig [8] in 88% yield, the highly insoluble potassium salt monohydrate had m.p. >200°, τ (CF$_3$·CO$_2$H) 2·66 (10H, m), 3·85 (1H, d, J 12 Hz), 5·2—6·6 (3H, 8 broad lines), and 7·77 (3H, s). Vorlander and Schrödter [3] record satisfactory analytical figures for the monohydrate, but we were unable to obtain a good analysis for the anhydrous salt [Found (after drying at 20° and 0·01 mmHg): C, 56·3, 56·5; H, 4·7, 4·8. Calc. for $C_{19}H_{17}KO_6S$: C, 55·3; H, 4·2%].

The sodium salt trihydrate [3] was prepared from the potassium salt monohydrate (8·6 g) by rapid dissolution in hot 50% acetic acid (100 ml), dilution with cold water (600 ml), and neutralisation with solid sodium carbonate. After recrystallisation from 50% aqueous methanol, the salt had m.p. *ca.* 240° (decomp.) (with previous brown discolouration), $\lambda_{max.}$ 301 nm (log ε 2·0), 265, 258, 253, and 248 nm (all log ε < 2·6), and end absorption down to 200 nm, $\nu_{max.}$ (KBr) 3400, 3040, 1765, 1720, 1370, 1220, 1075, and 1030 cm^{-1}; $\nu_{max.}$ (Nujol) 3480, 1760, 1230, and 1040 cm^{-1}; for n.m.r. and mass spectra see Discussion section [Found (after drying at 20° and 0·01 mmHg): C, 57·65, 57·7; H, 4·5, 4·4; S, 7·9, 8·0. Calc. for $C_{19}H_{17}NaO_6S$: C, 57·6; H, 4·3; S, 8·1%]. If boiling with acetic acid is prolonged, the free hydrogen sulphate decomposes to give a low yield (27%) of Vorlander's ketol (X), m.p. 175° (from methanol) (lit.,[3] 176°).

Reactions of the Acetoxydiphenylcyclopentenyl Sodium Sulphate (XI).—(a) *Alkaline hydrolysis.* The sodium salt

* Chloroform solutions give carbonyl frequencies *ca.* 15 cm^{-1} lower than those observed in carbon tetrachloride.[19]

[19] A. R. H. Cole, *Rev. Pure Appl. Chem.*, 1954, **4**, 119.

trihydrate (100 mg) in 50% aqueous ethanol (20 ml) was refluxed with sodium hydroxide (110 mg) for 1 h. The cooled solution, on acidification with 2N-sulphuric acid furnished colourless crystals; water (50 ml) was added and the suspension was set aside overnight, and filtered to yield 5-hydroxy-2,3-diphenylcyclopent-2-enone (Vorlander's ketol) (X) (62 mg, 96%), m.p. 175°, $\lambda_{max.}$ 303 nm (log ε 4·6), $\nu_{max.}$ 3475, 1690, 1638, 1380, and 1116 cm^{-1}; τ (CDCl$_3$) 2·73 (10H, m), 5·45, 6·8, and 7·6 (ABX pattern: J_{AX} 2, J_{BX} 7, and J_{AB} 19 Hz), and 3·3 (ca. 1H, exchangeable OH) (Found: M^+, 250. Calc. for $C_{17}H_{14}O_2$: M, 250). The acetate had m.p. 145° (lit.,[3] 145°); the red 2,4-dinitrophenylhydrazone had m.p. 240° (from methanol).

(b) *Catalytic hydrogenation.* The sodium salt trihydrate (150 mg) dissolved in methanol (80 ml) was shaken with platinum oxide (30 mg) in hydrogen until absorption ceased. Filtration and evaporation of the filtrate in a vacuum gave a highly insoluble colourless sodium salt (140 mg), m.p. 240—245° (decomp.), $\nu_{max.}$ (KBr) 3020, 1732, 1365, and 1245 cm^{-1}, τ (CF$_3$·CO$_2$H) 2·7 (10H, m), 4·9—7·0 (unresolved multiplets), and 7·8 (3H, s). The product thus contained an acetyl group, but hydrolysis with potassium carbonate in hot 50% aqueous methanol, followed by reduction with lithium aluminium hydride–aluminium chloride, gave no identifiable product.

(c) *Reduction with hydriodic acid.* The sodium salt trihydrate (100 mg) was refluxed with 48% hydriodic acid (d 1·6; 15 ml) and red phosphorus (100 mg) for 8 h. The cooled mixture was diluted and filtered, and the precipitate was washed with chloroform; the filtrate was extracted thrice with chloroform (25 ml). The washings and extracts were combined, washed with water, dried, and evaporated in a vacuum. The product (38·5 mg) exhibited $\nu_{max.}$ 3080 and 1690 cm^{-1}. Samples were analysed by g.l.c. on an XE60 column to give: (i) cis-1,2-diphenylcyclopentane (VI) (0·1%; t_R 5·6 min), (ii) trans-1,2-diphenylcyclopentane (XII) (46%; t_R 6·4 min), (iii) an unidentified compound, not cleanly separable from (ii), regarded as a diphenylcyclopentene (XIII?) (16%; t_R ca. 7 min), and (iv) an unidentified diphenylcyclopentenone (XIV?) (29%; t_R 14·8 min). In a similar experiment run for 20 h the products were (i) 0·03—0·06%, (ii) 71%, (iii) 21%, and (iv) 2%, with an additional component (v) (5%), t_R 12·9 min, similar to that of trans-3,4-diphenylcyclopentanone (VII). Authentic samples of cis-1,2-diphenylcyclopentane, m.p. 45° (lit.,[7,10] 46—47°) and of trans-1,2-diphenylcyclopentane, m.p. 60° (lit.,[7,10] 65°, shown by g.l.c. to be 94% pure), gave retention times identical with those of (i) and (ii) when examined alone or mixed with the crude reduction product. 3,4-Diphenyl-cyclopent-2-enone [15] (XIV), m.p. 108°, $\nu_{max.}$ 1710, 1680, 1600, and 1567 cm^{-1}, prepared from anhydracetonebenzil (4-hydroxy-3,4-diphenylcyclopent-2-enone) [14] by reduction with 48% hydriodic acid and red phosphorus in fluxing acetic acid for 1 h, exhibited t_R 14·8 min.

Reduction of trans,trans-1,5-*Diphenylpenta-1,4-dien-3-one* (I) *with Hydriodic Acid.*—(a) The ketone (I) (5 g) was refluxed with 48% hydriodic acid (d 1·6; 50 ml) and red phosphorus (5 g) for 24 h. The cooled solution was thrice extracted with chloroform (25 ml); the extracts were washed with water, dried, evaporated under reduced pressure. The resulting orange oil (5·4 g) had $\nu_{max.}$ 1735, 1708, and 1680sh cm^{-1}; g.l.c. analysis of a sample showed the presence of trans-3,4-diphenylcyclopentanone (VII)

(266 mg; estimated from the peak area by comparison with a standard curve given by a genuine specimen, for the whole product). The orange oil on column chromatography on neutral alumina in hexane [elution with hexane, benzene, ether, chloroform, and mixtures thereof (500 ml fractions)] gave six fractions (total wt. 3·24 g); final elution with methanol gave no material. Those fractions exhibiting $\nu_{max.}$ 1735 and 1708 cm^{-1} were subjected to preparative g.l.c. to yield trans-3,4-diphenylcyclopentanone (VII), m.p. 173—175° (lit.,[7,10] 177°), $\nu_{max.}$ 1735 and 1595 cm^{-1}, characterised as the 2,4-dinitrophenylhydrazone, m.p. 169—170° (lit.,[10] 170°) (Found: M^+, 236. Calc. for $C_{17}H_{16}O$: M, 236). The other fractions (3·1 g) were united; crystallisation from methanol or carbon tetrachloride yielded a dimeric species (XVIII?), m.p. 185°, $\nu_{max.}$ 1708, 1670, and 1600 cm^{-1}, m/e 472, 351 (base peak), 367, 339, 325, 237, 131, and 91 (Found: C, 85·5; H, 6·9. Calc. for $C_{34}H_{32}O_2$: C, 86·4; H, 6·8%; M, 472), yielding a yellow 2,4-dinitrophenylhydrazone, m.p. 212—215° (from chloroform–ethanol).

(b) The ketone (5·0 g) dissolved in acetic acid (40 ml) was refluxed with 48% hydriodic acid (d 1·6; 1·5 ml) and red phosphorus (2·5 g) for 24 h. The hot mixture was filtered into dilute aqueous sodium hydrogen sulphite solution, and the product was extracted with chloroform (4 × 25 ml). The extract was washed with N-sodium hydroxide and water, dried (K$_2$CO$_3$), and evaporated in a vacuum. The red oil (4·9 g) exhibited $\nu_{max.}$ 1735 and 1708 cm^{-1}, and slowly crystallised. G.l.c. analysis of a sample showed the presence of trans-3,4-diphenylcyclopentanone (VII) (625 mg, 13%, estimated from the peak area by comparison with a standard curve given by an authentic sample, for the whole product). The main product (4·27 g, 84% yield) presumably consisted of the dimeric species (XVIII?) and possibly higher polymeric compounds.

APPENDIX (By C. W. Shoppee)

3-Methylenepenta-1,4-diene ($\equiv$ 3-vinylbuta-1,3-diene) has been used as a model six π-electron system (A) for
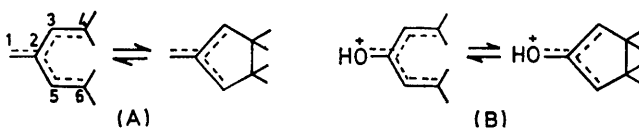
SCHEME A

comparison with the six π-electron system (B) (Scheme A). The MO's of the acyclic member of the pair (A) with coefficients are given by Streitwieser [20] and may be represented as in Table A. The MO's of the cyclic partner of interest are as in Table B. If the MO's π_2 and π_3 are degenerate, and the singlet ground-state wave function contains an equal admixture of the configurations $\sigma^2\pi_1{}^2\pi_2{}^2$ and $\sigma^2\pi_1{}^2\pi_3{}^2$, the cyclisation process should be non-stereospecific. If the degeneracy of π_2 and π_3 is broken by terminal substituents, then cyclisation should be stereospecific, conrotatory if π_2 is lower in energy, and disrotatory if π_3 is lower in energy.

Introduction of a positively charged oxygen atom, as in system (B), will attract electrons from the pentadiene chain and from the cyclopentene ring. The energies of

[20] A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1960, pp. 51, 60, 61, 95, and 135.

the wave functions ψ_1 and ψ_3 for the 3-methylenepenta-1,4-diene molecule, $E_1 = \alpha + 1 \cdot 9\beta$ and $E_3 = \alpha + 0 \cdot 5\beta$,[21] will be decreased to $E'_1 = \alpha + 2 \cdot 2\beta$ and $E'_3 = \alpha + 1 \cdot 5\beta$ for the penta-1,4-dien-3-one cation [taking the Coulomb integral h_{O^+} as 2·5 (ref. 20)]; the energy of the wave function ψ_2 will be the same, $E_2 = E'_2 = \alpha + 1 \cdot 0\beta$,[21] for the molecule and the cation because of the symmetrically located single node. In brief, the highest filled MO in the

of the forms of the wave functions ψ_2 and ψ_3 for the 3-methylenepenta-1,4-diene molecule shows that only ψ_3 has electron density at C-1, so that substitution of oxygen for that carbon atom should not affect ψ_2 but should stabilise ψ_3, putting ψ_3 at lower energy than ψ_2; similarly, inspection of the forms of the wave functions π_2 and π_3 for the cyclic member of system (A) shows that only π_2 has electron density at C-1, so that substitution of oxygen

TABLE A

orbital symmetry	C_2^z	σ^{xz}	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
C_2^z			a	s	a	a	s	a
σ^{xz}			s	a	s	s	a	s

TABLE B

orbital symmetry	σ	π_1	π_2	π_3	π_4	σ^*
C_2^z	s	a	a	s	a	a
σ^{xz}	s	s	s	a	s	a

acyclic cation of system (B) will be ψ_2. Similarly, the energies of the wave functions π_1 and π_2 for the cyclic member of system (A) will be decreased for the cyclo-

FIGURE

pentenyl cation of system (B), whilst π_3 will be unchanged; probable values are $E'_1 = \alpha + 1 \cdot 5\beta$, $E'_2 = \alpha + 1 \cdot 2\beta$, $E_3 = E'_3 = \alpha + 0 \cdot 0\beta$. These conclusions can also be reached by a perturbation argument; inspection
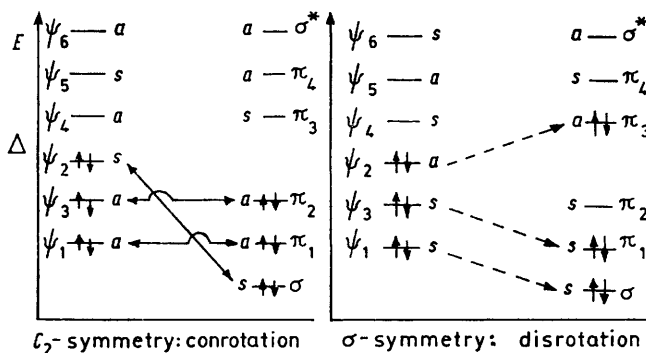
for that carbon atom should not affect π_3 but will stabilise π_2.

These considerations lead to the illustrated orbital symmetry correlation diagrams for system (B) (Figure). Thus the cationic six π-electron system (B) should undergo a conrotatory thermal ground-state reaction, $\psi_1{}^2\psi_3{}^2\psi_2{}^2 \rightleftharpoons \sigma^2\pi_1{}^2\pi_2{}^2$, which is symmetry-allowed and energetically favourable; the corresponding disrotatory cyclisation, $\psi_1{}^2\psi_3{}^2\psi_2{}^2 \rightleftharpoons \sigma_2{}^2\pi_1{}^2\pi_3{}^2$, is symmetry-forbidden.

[21] C. A. Coulson and A. Streitwieser, jun., 'Dictionary of π-Electron Calculations,' Freeman, 1965, p. 3.