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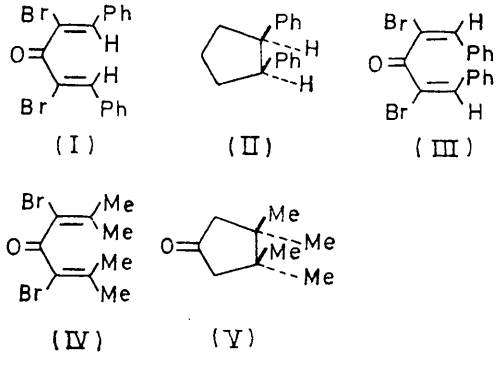
Electrocyclic Reactions. Part IV.[1] Some Reactions of 2,4-Dibromo-1,5-diphenylpenta-1,4-dien-3-one (αα′-Dibromodibenzylideneacetone)

By **Charles W. Shoppee** * and **Burgess J. A. Cooke**, Department of Chemistry, Texas Technological University, Lubbock, Texas 79409, U.S.A.

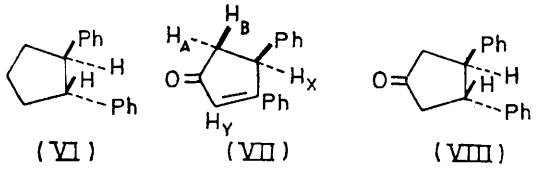
Treatment of αα′-dibromodibenzylideneacetone (I) with hot hydriodic acid and red phosphorus has been claimed to yield 60% of *cis*-1,2-diphenylcyclopentane; in fact, the product consists of *trans*-3,4-diphenylcyclopentanone (24%), which is not reduced by the reagent, 3,4-diphenylcyclopent-2-enone (5%), which is reduced by the reagent to a mixture of *cis*-1,2-diphenylcyclopentane and a little *trans*-1,2-diphenylcyclopentane, and a polymeric hydrocarbon of unknown structure (*ca.* 25%). Treatment of the dibromo-ketone (I) with cold concentrated sulphuric acid furnishes 3-bromo-2-hydroxy-*trans*-4,5-diphenylcyclopent-2-enone (10%) and *trans*-2,5-dibromo-3,4-diphenylcyclopent-2-enone (85%). The primary cyclic products appear to arise by thermal ground state concerted conrotatory [2 + 2] electrocyclic reactions.

In 1914, Hellthaler[2] reported that reduction with hydriodic acid of αα′-dibromodibenzylideneacetone (I) (obtained from *trans,trans*-dibenzylideneacetone[3] by conversion into the tetrabromide and dehydrobromination with pyridine at 20° or with hot ethanolic potassium acetate[2]) gives a 60% yield of *cis*-1,2-diphenylcyclopentane (II). This report[2] recalls the reduction by Ingold and Shoppee[4] of αα′-dibromophorone (IV) with hydriodic acid to give 3,3,4,4-tetramethylcyclopentanone (V), regarded by Shoppee and Lack[5] as the product of a thermal ground state conrotatory [2 + 2] electrocyclic reaction with the stereochemistry of the cyclisation process masked by the equivalence of the four terminal methyl groups. If the assignment of the *trans,trans*(Br/H)-configuration to the dibromo-ketone (I) is correct, conversion of the *s-trans,trans*-conformation into a precursor of *cis*-1,2-diphenylcyclopentane (II) would involve a concerted disrotatory [2 + 2] cyclisation process and would appear to violate the Woodward–Hoffmann rules for conservation



of orbital symmetry,[6] which predict conrotation (see Appendix). If the dibromo-ketone has the *cis,cis*-(Br/H)-configuration (III), its conversion into *cis*-1,2-diphenylcyclopentane would also involve a disrotatory process and violate the rules.

We find that the product of the reaction of the dibromo-ketone (I) with hydriodic acid under Hellthaler's conditions[2] is a complex mixture of cyclic compounds (57—68% yield) together with a polymeric hydrocarbon, m.p. 143° (*ca.* 25%). Analysis of the product by column chromatography followed by g.l.c. against authentic samples showed the presence of *cis*-1,2-diphenylcyclopentane[2,7] (II), m.p. 47°, *trans*-1,2-diphenylcyclopentane[7] (VI), m.p. 65°, 3,4-diphenylcyclopent-2-enone[1,8] (*cf.* ref. 9) (VII), m.p. 108°, $\nu_{max.}$ 1710 and 1680 cm^{-1}, and *trans*-3,4-diphenylcyclopentanone[1,7,10] (VIII), m.p. 173°, $\nu_{max.}$ 1735 cm^{-1}. The structures of compounds (II), (VI), (VII), and (VIII) are established; that of



(VII) is consistent with the n.m.r. spectrum, which is identical with that of material prepared from 4-hydroxy-3,4-diphenylcyclopent-2-enone by reduction with hydriodic acid and red phosphorus[8] by the procedure of Geissman and Koelsch,[11] and shows an ABX pattern of signals at δ 2·40 (H_A), 3·13 (H_B), 4·67 (H_X) (J_{AB} 19, J_{AX} 2, and J_{BX} 7 Hz), a doublet at 6·80 for the vinyl proton H_Y coupled allylically to H_X (J 1·5 Hz), and a multiplet centred at δ 7·3 (10H, aromatic).

A selection of our results is collected in the Table; the *trans*-hydrocarbon (VI) is not converted into the *cis*-hydrocarbon (II) under our experimental conditions. The yields of the hydrocarbons (II) and (VI) from the dibromo-ketone (I) show no regular or readily explicable time dependence. The yield of the cyclopentanone (VIII) formed from (I) increases by 7% if the time is

[1] Part III, C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1973, 1026.
[2] G. Hellthaler, *Annalen*, 1914, **406**, 161.
[3] J. G. Dinwiddie, jun., H. M. White, and W. J. Day, *J. Org. Chem.*, 1962, **27**, 327.
[4] C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1928, 365.
[5] C. W. Shoppee and R. E. Lack, *J. Chem. Soc.* (*C*), 1969, 1346.
[6] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, 1970, 45.
[7] H. A. Weidlich, *Ber.*, 1938, **71**, 1601.
[8] P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Amer. Chem. Soc.*, 1958, **80**, 202.
[9] F. R. Japp and G. D. Lander, *J. Chem. Soc.*, 1897, **71**, 123.
[10] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1939, 567.
[11] T. A. Geissman and C. F. Koelsch, *J. Org. Chem.*, 1939, **3**, 489.

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extended from 8 to 24 h, whereas that of the cyclopentenone (VII) decreases by 6%; under the same conditions, however, the cyclopentenone (VII) is not reduced to the cyclopentanone (VIII). We have shown [12] that the cyclopentanone (VIII) is not reduced by refluxing 48% hydriodic acid and red phosphorus

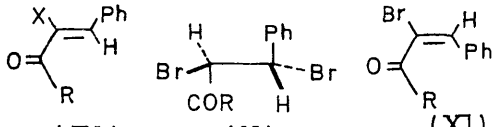
Reductions with refluxing 48% hydriodic acid

Compound	Time (h)	(II) (%)	(VI) (%)	(VII) (%)	(VIII) (%)	Total yield (%)
(I)	8	11	29	11	17	68 *
	24	15	13	5	24	57 *
	8 †	0·8	0·2	48	49	98
	24 †	4·5	0·5	42	50	97
(VII)	24	73	5	0	0	78
	10 ‡	24	1·5	14	0	40

* A polymeric hydrocarbon, m.p. 143°, involatile on g.l.c., was also isolated in *ca.* 25% yield. † In a 10% solution of 48% hydriodic acid in acetic acid. ‡ In a 25% solution of 48% hydriodic acid in acetic acid.

to *trans*-1,2-diphenylcyclopentane (VI). Reduction of the cyclopentenone (VII) appears to be responsible for the formation of both the *cis*-hydrocarbon (II) and the *trans*-hydrocarbon (VI) in the cyclisation of the dibromo-ketone (I). We can thus account for the production from the dibromo-ketone (I) of *cis*-1,2-diphenylcyclopentane (II) reported by Hellthaler,[2] but not for his claimed 60% yield of crude material; Hellthaler's hydrocarbon was isolated by steam distillation of the reaction mixture (both the *cis*- and the *trans*-hydrocarbon are volatile in steam [7]) and crystallisation of the solidified distillation product from ethanol–acetone–water (with possible loss of any *trans*-hydrocarbon); presumably any cyclopentenone (VII) and cyclopentanone (VIII) remained in the residue, which was not further examined. The total yields of hydrocarbons (II) and (VI) formed by cyclisation of the dibromo-ketone (I) are lower (40 and 28%) than that obtained by reduction of the cyclopentenone (VII) (78%), and the *cis* : *trans*-hydrocarbon ratios resulting from cyclisation (1 : 2·7 and *ca.* 1 : 1) are lower than the ratio resulting from reduction (15 : 1). Hydriodic acid–red phosphorus reductions have long been used in structure determination, and are a fairly general method for reduction of alcohols [13,14] to the corresponding hydrocarbons; that such reductions are heterogeneous reactions may account for the lack of reproducibility of our product ratios (*cf.* Table and Experimental section), and for the fact that their mechanism is incompletely understood.[15] The dibromo-ketone (I) is soluble in acetic acid, which has been used as a medium,[10,11] as also has acetic anhydride,[16] for hydriodic acid–phosphorus reductions; we therefore examined the cyclisation of the dibromo-ketone (I) under these homogenous conditions. As shown in the Table the material balance then became virtually quantitative; the cyclopentenone (VII) and the cyclopentanone (VIII) were formed in the ratio of *ca.* 1 : 1, along with small amounts of the *cis*- and *trans*-hydrocarbons (II) and (VI) (1 and 5%), for which the *cis* : *trans*-ratio increases with time (4 : 1 ⟶ 9 : 1). The results indicate that the cyclopentenone (VII) is relatively inert to further reduction by a 10% solution of 48% hydriodic acid in acetic acid; to achieve substantial reduction of the cyclopentenone (VII) the proportion of 48% hydriodic acid has to be raised from 10 to 25%, but the *cis*-hydrocarbon (II) still predominates over the *trans*-hydrocarbon (VI) (16 : 1).

We have tried to establish the configuration of αα′-dibromodibenzylideneacetone,[2] m.p. 97°, which is homogeneous by t.l.c. in several solvent systems but involatile on g.l.c. It has not proved possible to obtain suitably large crystals for an *X*-ray investigation. We attempted Baeyer–Villiger oxidation of (I) with trifluoroperacetic anhydride in refluxing chloroform (*cf.* ref. 17) followed by mild alkaline hydrolysis but failed to isolate an α-bromocinnamic acid. *trans,trans*-Dibenzylideneacetone, on *trans*-addition of bromine followed by *trans*-elimination of hydrogen bromide, should yield the *cis,cis*(Br/H)-isomer (III). Thus the reported addition of bromine to benzylideneacetone (IX; X = H, R = Me) and to benzylideneacetophenone (chalcone) (IX; X = H, R = Ph) gives the *erythro*-dibromides (X; R = Me or Ph), which when subjected to base-catalysed elimination of hydrogen bromide yield initially, under kinetic control, the *cis*-α-bromo-ketones (XI; R = Me or Ph).[18,19] Treatment of the



(IX) (X) (XI)

dibromide (X; R = Ph) with sodium acetate in dimethylformamide at 25° gave only the *cis*-α-bromo-ketone (XI: R = Ph), but use of sodium acetate in refluxing ethanol gave a mixture (34 : 66) of *cis*-α-bromo-ketone (XI; R = Ph) and *trans*-α-bromo-ketone (IX; X = Br, R = Ph); heating the *cis*-α-bromo-ketone (XI; R = Ph) at 160° resulted in significant isomerisation under thermodynamic control to the *trans*-α-bromo-ketone (IX; X = Br, R = Ph).[18] Treatment of the dibromide (X; R = Me) with sodium

[12] C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1972, 2271.
[13] G. D. Meakins and R. Swindells, *J. Chem. Soc.*, 1959, 1044.
[14] A. C. Cope, R. K. Bly, E. P. Burrows, O. J. Ceder, E. Ciganek, B. T. Gillis, R. F. Porter, and H. E. Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 2170.
[15] L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1968, 449, 862, 865, and references cited therein.
[16] H. B. Gillespie and H. R. Snyder, *Org. Synth.*, Coll. Vol. II, 1943, 489.
[17] G. R. Pettit, P. Hofer, W. J. Bowyer, T. R. Kasturi, R. C. Bansal, R. E. Kadunce, and B. Green, *Tetrahedron*, 1963, **19**, 1143.
[18] R. E. Lutz, D. F. Hinkley, and R. H. Jordan, *J. Amer. Chem. Soc.*, 1951, **73**, 4647.
[19] A. Hassner, G. L'abbe, and M. J. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 981.

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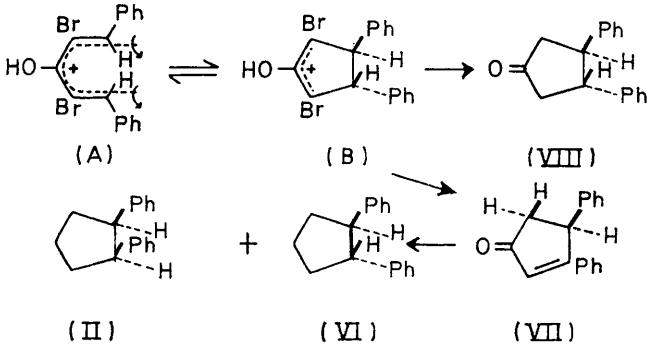
acetate in dimethylformamide at 25° gave a mixture (60 : 40) of *cis*-α-bromo-ketone (XI; R = Me) and *trans*-α-bromo-ketone (IX: X = Br, R = Me); the *cis*-α-bromoketone (XI: R = Me) was isomerised completely to the *trans*-α-bromo-ketone (IX; X = Br, R = Me) by treatment with sodium azide in dimethylformamide at 25° for 15 min, or with iodine in chloroform at 65° for 4 h.[19] Thus it seems probable that sequential bromination and dehydrobromination of *trans,trans*-dibenzylideneacetone initially gives the *cis,cis*-dibromoketone (III), but that this isomerises completely under our reaction conditions (pyridine at 50—60° for 48 h or sodium acetate in refluxing ethanol) to the *trans,trans*-isomer (I).

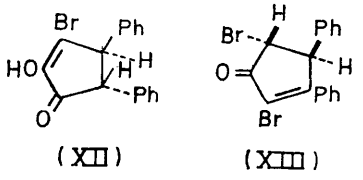
trans,trans-Dibenzylideneacetone exists in the *s-cis,cis*-conformation,[8] whereas αα′-dimethyldibenzylideneacetone exists preferentially in the *s-trans,trans*-conformation[1,8] because of the unfavourable 1,3-methyl/methyl interaction in the *s-cis,cis*-conformation (van der Waals radius of methyl,[20] 2·0 Å). It therefore seems probable that αα′-dibromodibenzylideneacetone exists preferentially in the *s-trans,trans*-conformation (I) (van der Waals radius of bromine,[20] 1·95 Å). Comparison of the



u.v. maxima of the dibromo-ketone [312 nm (log ε 4·24)] and *trans,trans*-dibenzylideneacetone (*s-cis,cis*-conformation)[8] [330 nm (log ε 4·54)] with those of *trans*-1-benzylidene-1-bromoacetone[21] (IX; X = Br, R = Me) [295 nm (log ε 4·25); Δλ 17 nm] and benzylideneacetone[22] (IX; X = H, R = Me) [286 nm (log ε 4·37); Δλ 44 nm], having regard to the increment for the second α-bromo-substituent[23] (Δλ 23 nm), also suggests that the dibromo-ketone exists in the *s-trans,trans*-conformation (I) in solution.

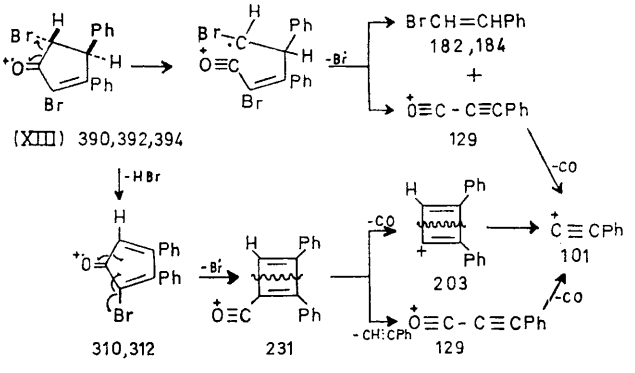
Although the results can be interpreted in terms of formulae (I) or (III), we believe that the dibromo-ketone (I), as the pentadienyl cation (A), undergoes a thermal ground state concerted conrotatory [2 + 2] electrocyclic reaction to yield the cyclopentenyl cation (B), which by elimination of a proton and reductive removal of both bromine atoms affords 3,4-diphenylcyclopent-2-enone (VII), or furnishes directly by reduction *trans*-3,4-diphenylcyclopentanone (VIII). The cyclopentenone (VII) by further reduction yields both *cis*-1,2-diphenylcyclopentane (II) and *trans*-1,2-diphenylcyclopentane (VI); the cyclopentanone (VIII) retains and reveals the stereochemistry of the cyclisation process to the extent of 17—24%.

We have also investigated the action of concentrated sulphuric acid at 25° on the dibromo-ketone (I); this leads to an alkali-soluble hydroxy-bromo-ketone (XII) (10%) and an unsaturated dibromo-ketone (XIII)



(85%). The structure of the quasi-acidic 3-bromo-2-hydroxy-*trans*-4,5-diphenylcyclopent-2-enone (XII) is supported by the i.r., n.m.r., and mass spectra. The n.m.r. spectrum shows an AB quartet at δ 4·13 and 5·65 (2H, *J* 2·7 Hz) and a complex multiplet centred at δ 2·62 (10 aromatic and a single enolic proton). The field-ionisation mass spectrum shows a pair of isotopic parent peaks, M^+ 328 and 330 (intensities 1 : 1), not shown by the electron-impact mass spectrum, which however exhibits a pair of isotopic peaks at *m/e* 327 and 329 (intensities 1 : 1) (*M* — H), a base peak at *m/e* 249 (*M* — Br), and a structurally consistent fragmentation pattern [*m/e* 231, 221, 203, and 178 (PhC≡CPh)].

The structure of the yellow *trans*-2,5-dibromo-3,4-diphenylcyclopent-2-enone (XIII) follows from the i.r., n.m.r., and mass spectra. The n.m.r. spectrum shows an AB quartet at δ 4·30 and 4·69 (2H, *J* 2·3 Hz), and a



SCHEME

complex multiplet centred at δ 2·76 (10H, aromatic). The mass spectrum shows a cluster of three isotopic parent peaks, M^+ 390, 392, and 394 (intensities 1 : 2 : 1), an isotopic pair of peaks at *m/e* 310 and 312 (intensities 1 : 1), and a supporting fragmentation pattern (Scheme).

[20] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, p. 28.
[21] J. Klein and S. Zitrin, *J. Org. Chem.*, 1970, **35**, 666.
[22] A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson, and C. H. Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985.
[23] J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, New Jersey, 1965, pp. 11—13.

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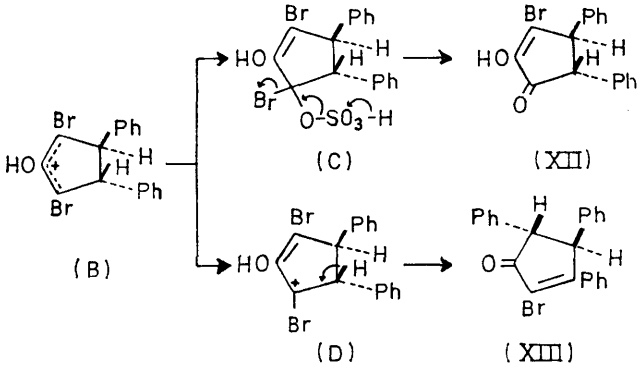
Reduction of the unsaturated dibromo-ketone (XIII) by refluxing with a 10% solution of 48% hydriodic acid in acetic acid and red phosphorus gave the cyclopentenone (VII) in 59% yield, together with traces of the cyclopentanone (VIII) (0·3%) and the *cis*- and *trans*-hydrocarbons (II) and (VI) (0·5%). The virtual absence of the *trans*-ketone (VIII) from these reduction products furnishes further evidence for the assertion that (VIII) is formed by direct reduction of cation (B), rather than by elimination followed by subsequent reduction.

We believe that the cyclopentadienyl cation (B), as the hydrogen sulphate (C), eliminates hydrogen bromide and sulphur trioxide by a concerted process to afford the hydroxy-bromo-ketone (XII), or, as the canonical form (D), loses a benzylic proton to yield the unsaturated dibromo-ketone (XIII). We attribute the nearly



quantitative yield of the products (XII) and (XIII) to the irreversibility of the cyclisation process [(A) $\rightleftharpoons$ (B) $\equiv$ (D)] caused by elimination of hydrogen bromide from the hydrogen sulphate (C) and by depolarisation of the carbonium ion (D). The formation of the unsaturated dibromo-ketone (XIII) in 85% yield appears to be good evidence for the occurrence of the cyclopentenyl cation [(B) $\equiv$ (D)]. It seems likely that the unsaturated dibromo-ketone (XIII), or its enolic form, is an intermediate in the hydriodic acid-catalysed electrocyclisation of the dibromo-ketone (I).

EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345. M.p.s were determined with a Thomas 40 hot-stage apparatus, and are corrected. U.v. spectra (ethanolic solution) 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 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). 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 either with a Beckman GC45 chromatograph fitted with a flame ionisation detector and a 6 ft × 1/8 in column packed with 5% XE60 substrate (helium flow rate of 40 ml min^{-1}; temperature programming from 100 to 200°), or, for preparative injections, with an Aerograph Autoprep 700, using columns of Carbowax 20M (for hydrocarbons) or SE30 (for ketones).

2,4-*Dibromo*-1,5-*diphenylpenta*-1,4-*dien*-3-*one* (I).—Prepared from *trans,trans*-dibenzylideneacetone by conversion into the tetrabromide and dehydrobromination of this with pyridine at 60°, the dibromo-ketone (70% yield) had m.p. 96—97·5° (from methanol) (lit.,[2] 97—97·5°; lit.,[25] 98°), $\lambda_{max.}$ 312 (log ε 4·24) and 257 nm (4·10), $\nu_{max.}$ 1660, 1590, and 1570 cm^{-1}, δ [$CDCl_3$–$(CD_3)_2SO$] 7·39 and 7·83 (complex multiplets); homogeneous by t.l.c. on silica (R_F 0·2, 0·8, and 1·0 in hexane, benzene–hexane, and benzene); involatile by g.l.c. on SE30, XE60, and Carbowax 20M columns.

Treatment of the Dibromo-ketone (I) *with Trifluoroperacetic Anhydride.*—The dibromo-ketone (I) (280 mg), dissolved in chloroform, was refluxed with a solution of trifluoroperacetic anhydride in methylene chloride (0·8 ml) [prepared from trifluoroacetic anhydride (12 ml), and 90% hydrogen peroxide (1·6 ml) in methylene chloride (10 ml) [17]] for 8 h. The cooled mixture was washed with several portions of water, and the product was isolated in the usual way; the resultant red oil (245 mg) had an i.r. spectrum similar to that of the starting material. Attempted hydrolysis of the product with aqueous methanolic sodium hydroxide solution gave oily products, whose n.m.r. spectra indicated the absence of an α-bromocinnamic acid.[21]

Reduction of the Dibromo-ketone (I) *with Hydriodic Acid and Red Phosphorus.*—(a) *Without solvent.* The dibromo-ketone (3·5 g) was refluxed with 48% hydriodic acid (*d* 1·7; 25 ml) and red phosphorus (3·5 g) with stirring for 20 h. The mixture was cooled and filtered, and the residual solids were extracted with ether and with chloroform; the filtrate was extracted thrice with chloroform (3 × 20 ml). The combined extracts were washed with sodium thiosulphate solution, and with water, dried (K_2CO_3) and evaporated *in vacuo*. Column chromatography of the resulting orange solid (1·93 g) on alumina in hexane (elution with hexane, carbon tetrachloride, benzene, and ether) gave three fractions: (a) hydrocarbons (i) and (ii) (576 mg); (b) an orange oil (490 mg), which crystallised partially and after several recrystallisations from carbon tetrachloride–hexane gave material, m.p. 143—145°, showing an i.r. spectrum virtually identical with those of *cis*- (II) and *trans*-1,2-diphenylcyclopentane (VI); this substance was involatile on g.l.c. and was not further investigated; (c) ketones consisting of (iii) *trans*-3,4-diphenylcyclopentanone (VIII) (528 mg), m.p. 173° (lit.,[10] 175°), $\nu_{max.}$ 1735 cm^{-1}, yielding a 2,4-dinitrophenylhydrazone, m.p. 168—170° (lit.,[10] 170°), and (iv) 3,4-diphenylcyclopent-2-enone (VII) (98 mg), m.p. 106—108° (lit.,[8] 108—110°), $\nu_{max.}$ 1710 and 1680 cm^{-1} (lit.,[8] 1715 and 1689 cm^{-1}), δ 2·40, 3·13, and 4·67 (ABX pattern, J_{AB} 19, J_{AX} 2, J_{BX} 7 Hz), 6·80 (d, 1 vinyl H, *J* 1·5 Hz), and 7·3 (m, 10 ArH). Samples of fractions (a) and (c) were analysed by preparative g.l.c.

* Chloroform solutions give carbonyl bands *ca.* 15 cm^{-1} lower than those observed in carbon tetrachloride.[24]

[24] A. R. H. Cole, *Rev. Pure Appl. Chem.*, 1954, **4**, 119.
[25] S. Sugden, *J. Chem. Soc.*, 1928, 415.

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on an XE60 column to give: (i) *cis*-1,2-diphenylcyclopentane (II) (15·4%; t_R 5·6 min), m.p. 44—45° (from aqueous acetone) (lit.,[7,10] 46—47°), $\nu_{max.}$ 3070, 3030, 1595, and 683 cm^{-1}; (ii) *trans*-1,2-diphenylcyclopentane (VIII) (12·6%; t_R 6·4 min), m.p. 60° (lit.,[7,10] 65°). In a similar experiment using 0·7 g of the dibromo-ketone and a reaction time of 8 h, the products (g.l.c. analysis on an XE60 column) were: (II) (42 mg, 10·5%), (VI) (113 mg, 28·5%), (VIII) (73 mg, 17%), (VII) (46 mg, 11%), and involatile polymeric hydrocarbon (*ca.* 25%). Authentic specimens of the hydrocarbons (II) and (VI), prepared by Clemmensen reduction of *cis*-[7] and *trans*-3,4-diphenylcyclopentanone[7] (VIII), and of 3,4-diphenylcyclopent-2-enone (VII), prepared in 60% yield by reduction with hydriodic acid and red phosphorus[8,11] of 4-hydroxy-3,4-diphenylcyclopent-2-enone, had retention times identical with those of the products (i—iv) (alone or by co-injection).

(b) *In acetic acid.* The dibromo-ketone (311 mg) and red phosphorus (290 mg) were refluxed with stirring with a 10% solution of 48% hydriodic acid in acetic acid (15 ml). After 8 h a sample (5 ml) was withdrawn, added to saturated sodium hydrogen carbonate solution (400 ml), and extracted with chloroform (3 × 50 ml); the product (g.l.c. on an XE60 column) gave: (i) *cis*- and *trans*-3,4-diphenylcyclopentane (II) and (VI) (0·7 mg, 1%; *cis* : *trans* ratio 4 : 1), (ii) 3,4-diphenylcyclopent-2-enone (VII) (38 mg, 48%), and (iii) 3,4-diphenylcyclopentanone (VIII) (39 mg, 49%). The remainder of the reaction mixture was refluxed for a further 16 h, worked up, and analysed similarly to give: (i) *cis*- and *trans*-3,4-diphenylcyclopentane (II) and (VI) (6 mg, 5%; *cis* : *trans* ratio 9 : 1), (ii) 3,4-diphenylcyclopent-2-enone (VII) (45·7 mg, 42%), and (iii) 3,4-diphenylcyclopentanone (VIII) (55·4 mg, 50%).

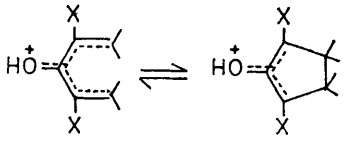
Reduction of 3,4-*Diphenylcyclopent*-2-*enone* (VII) *with Hydriodic Acid and Red Phosphorus.*—(a) *Without solvent.* The unsatuated ketone (107 mg) and red phosphorus (100 mg) were refluxed with 48% hydriodic acid (15 ml) with stirring for 24 h. The cooled mixture was diluted with water (100 ml) and filtered; the filtrate was extracted with ether–chloroform (3 × 25 ml). The extract was washed with sodium thiosulphate solution and with water, dried (K_2CO_3), and evaporated. The resultant oil (90 mg) was shown by g.l.c. analysis to comprise *cis*-1,2-diphenylcyclopentane (II) (67·4 mg, 73%) and *trans*-1,2-diphenylcyclopentane (VI) (4·5 mg, 5%) (*cis* : *trans* ratio 94 : 6). In similar experiments, the unsaturated ketone (500 and 100 mg) under apparently identical conditions yielded differently constituted mixtures of hydrocarbons [(II) (13 and 14 mg, 3 and 15%) and (VI) (72 and 40 mg, 15 and 13%)] with different *cis* : *trans* ratios (1 : 6 and 1·2 : 1) along with some starting material (6 and 2%). In another run for 8 h, the unsaturated ketone (100 mg) gave a mixture of hydrocarbons (II) (3 mg, 3%) and (VI) (21 mg, 23%) (*cis* : *trans* ratio 1 : 8), and starting material (11 mg, 11%).

(b) *In acetic acid.* The unsaturated ketone (100 mg), red phosphorus (103 mg), 48% hydriodic acid (5 ml), and acetic acid (15 ml) were refluxed with stirring for 10 h; the product was worked up and analysed by g.l.c. to give a mixture of hydrocarbons (II) (24 mg, 24%) and (VI) (1·5 mg, 1·5%) (*cis* : *trans* ratio 95 : 5), and starting material (14 mg, 14%).

Reaction of the Dibromo-ketone (I) *with Concentrated Sulphuric Acid.*—The dibromoketone (I) (1·42 g) was slowly added to concentrated sulphuric acid (8 ml) at 0°; the solution was stirred at 0° for 15 min and then at 20° for 30 min. The mixture was poured on ice to yield a yellow solid, which was filtered off, washed with water, and dried in air overnight. The product was dissolved in ether and the solution washed with saturated potassium carbonate solution (3 × 50 ml), dried and evaporated to leave an orange oil (1·20 g, 85%), which crystallised. T.l.c. showed the presence of a single substance and the absence of starting material. Two recrystallisations from methanol–chloroform (1 : 1) afforded trans-2,5-*dibromo*-3,4-*diphenylcyclopent*-2-*enone* (XIII) as yellow needles, m.p. 104—106°, $\nu_{max.}$ 1723 cm^{-1}; for n.m.r. and mass spectra, see Discussion section (Found: C, 52·15; H, 3·2; Br, 40·7%; M^+, 390, 391·9273, 394. $C_{17}H_{12}{}^{79}Br^{81}BrO$ requires C, 52·1; H, 3·1; Br, 40·75%; *M*, 391·9231). Acidification of the potassium carbonate extracts with 2N-sulphuric acid yielded a quasi-acid (90 mg, 8% yield), which crystallised from methanol–chloroform (1 : 1) to give 3-*bromo*-2-*hydroxy*-trans-4,5-*diphenylcyclopent*-2-*enone* (XII), m.p. 152° (decomp.), $\nu_{max.}$ 3480, 1710, and 1660 cm^{-1}; for n.m.r. (in $CDCl_3$–CD_3CN) and mass spectra see Discussion section (Found: C, 62·2; H, 4·1; Br, 24·15%; M^+, 327, 329. $C_{17}H_{13}BrO_2$ requires C, 62·0; H, 4·0; Br, 24·25%; *M*, 328, 330).

Reduction of trans-2,5-*Dibromo*-3,4-*diphenylcyclopent*-2-*enone* (XIII) *with Hydriodic Acid and Red Phosphorus in Acetic Acid.*—The ketone (XIII) (114 mg) and red phosphorus (103 mg) were refluxed with 48% hydriodic acid (2 ml) and acetic acid (18 ml) with stirring for 6 h; the product was worked up in the usual fashion. The crude material showed $\nu_{max.}$ 1725 (CO of starting material), 1710, and 1680 cm^{-1}; g.l.c. analysis on an XE60 column showed the presence of a trace of the cyclopentanone (VIII) (0·34 mg, 0·3%), the cyclopentenone (VII) (40 mg, 59%), and traces of the *cis*- and *trans*-hydrocarbons (II) and (VI) (total 0·33 mg, 0·5%; *cis* : *trans* ratio 1 : 4).

APPENDIX (By C. W. Shoppee)



(A)

The cationic system (A; X = Br) could be regarded as a ten π-electron system, with each bromine substituent contributing by its electromeric effect two *p*-electrons from appropriate MOs of π-symmetry, and a Hückel calculation could be made. More simply, a perturbation argument shows that the appropriate bromine MOs of π-symmetry will interact with ψ_1, ψ_2, ψ_3 and with π_1, π_2, π_3, and that ψ_3 should be stabilised more than ψ_2 but that π_2 should be stabilised more than π_3. The orbital symmetry correlation diagrams previously given for a six π-electron system[12] thus appear to be valid, and the cationic ten π-electron system (A; X = Br) 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, whilst the corresponding disrotatory process, $\psi_1^2\psi_3^2\psi_2^2 \rightleftharpoons \sigma^2\pi_1^2\pi_3^2$ is symmetry-forbidden. Thus, as in the case of the system (A; X = H),[19] the system (A; X = Br) may be regarded as involving only four

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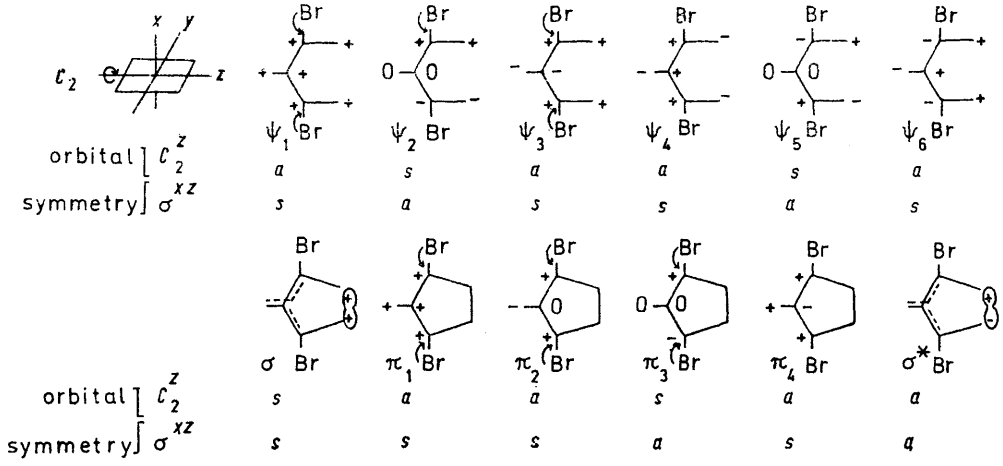

π-electrons, and, as now shown experimentally, undergoes thermal ground state conrotatory cyclisation.

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