Electrocyclic Reactions of Some Penta-1,4-diene Systems

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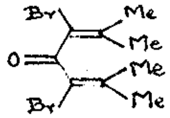
For Dr. Ken'ichi Takeda on the occasion of his 70th birthday.

A review of some thermal ground state and photochemical excited state reactions involving electrocyclisation of cations and anions derived from 1,5-diphenylpenta-1,4-diene systems.

The older chemical literature contains papers (published *inter alia* in 1903, 1904, 1914) describing the conversion of various acyclic penta-1,4-dienones by acidic reagents to derivatives of cyclopentane. Similarly, in 1928 the writer observed a pleasant camphoraceous odour during the reduction with phosphorus and hot hydriodic acid of the pentadienone αα'-dibromophorone (I); the compound responsible for the odour was isolated subsequently and shown (1) to be 3,3,4,4-tetramethylcyclopentanone (II).

(I)



(II)

In 1969 this transformation (I → II) was recognised (2) as involving a thermal ground state electrocyclic reaction in which stereochemistry is controlled by conservation of orbital symmetry as adumbrated in the Woodward-Hoffmann Rules (3). The four identical terminal groups in the system (I → II) prevent experimental distinction between conrotation and disrotation.

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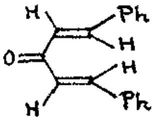
1 C.K. Ingold and C.W. Shoppee, *J. Chem. Soc.*, 1928, 365.

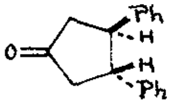
2 C.W. Shoppee and R.E. Lack, *J. Chem. Soc.* (*C*), 1969, 1346.

3 R.B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry', Academic Press, New York, 1970.

Other systems not suffering from this disability, e.g. the *trans*-*trans*-1,5-diphenylpenta-1,4-dienone system (III), have therefore been investigated, and a number of earlier observations of the formation of *trans*-3,4-diphenylcyclopentanone (IV) and its derivatives have been confirmed, the mechanisms elucidated, and new examples recorded.

(III)





(IV)

The selection rules for electrocyclic reactions and [m + n]cycloadditions of pentadiene systems (q = 1) are set out in Table 1.

Table 1

Number of π-electrons m + n	Thermally allowed, photochemically forbidden	Photochemically allowed, thermally forbidden
4q	Conrotatory m n $[{}_{\pi}2_{s} + {}_{\omega}0_{s} + {}_{\pi}2_{a}]$ $[{}_{\pi}2_{a} + {}_{\omega}0_{a} + {}_{\pi}2_{s}]$	Disrotatory m n $[{}_{\pi}2_{s} + {}_{\omega}0_{s} + {}_{\pi}2_{s}]$ $[{}_{\pi}2_{a} + {}_{\omega}0_{a} + {}_{\pi}2_{a}]$
4q + 2	Disrotatory m n $[{}_{\pi}2_{s} + {}_{\omega}2_{s} + {}_{\pi}2_{s}]$ $[{}_{\pi}2_{a} + {}_{\omega}2_{a} + {}_{\pi}2_{a}]$	Conrotatory m n $[{}_{\pi}2_{s} + {}_{\omega}2_{s} + {}_{\pi}2_{a}]$ $[{}_{\pi}2_{a} + {}_{\omega}2_{a} + {}_{\pi}2_{s}]$

Thermal conrotatory electrocyclisation of a pentadienyl cation (4q), photochemical electrocyclisation of a pentadienide anion (4q + 2), and corresponding cycloadditions, require that the original ethylenic components should ideally approach one another orthogonally in the transition state (3); however, as reaction proceeds these components become more and more tilted with respect to each other, and the initial geometry probably approximates to a 45° approach than a 90° approach. A twist angle of 42° has recently been suggested (4). The stereo-

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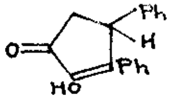
4 M.J.S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, 96, 6809.

chemical predictions contained in Table 1 have been confirmed for the systems described hereunder.

In 1903, Vorlander and Schrödter (5) found that trans-trans-1,5-diphenylpenta-1,4-dien-3-one (dibenzylideneacetone) (III) is stable to conc. sulphuric acid at 25°C and to acetic anhydride at 25°C, but is converted by treatment with conc. sulphuric acid and acetic anhydride at 25-30°C into a product regarded as an acetylated cyclopentenyl hydrogen sulphate, isolated as the sodium salt, $AcO{-}C_{17}H_{14}{-}OSO_3Na$, or the corresponding potassium salt, giving by mild alkaline hydrolysis Vorlander's ketol, $C_{17}H_{14}O_2$. In 1904, Vorlander and von Liebig (5) showed that reduction of the ketol with hydriodic acid and phosphorus gave cis-1,2-diphenylcyclopentane. In 1914, von Liebig (6) repeated the work of Vorlander and Schrödter and suggested formula (V) for the ketol. The cyclopentane ring structure must be present in the sodium salt, $AcO{-}C_{17}H_{14}{-}OSO_3Na$, since Metge (7) by reduction of this with sodium amalgam in acetic acid obtained trans-3,4-diphenylcyclopentanone (IV), a result that was confirmed in 1939 by Burton and Shoppee (8). In 1955, Allen, Van Allen, and Tinker (9) modified formula (V) for Vorlander's ketol to (VI) on account of the uv spectrum and the formation of an osazone and suggested structure (VII) for the sodium salt, $AcO{-}C_{17}H_{14}{-}OSO_3Na$.



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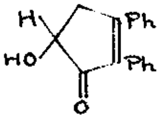
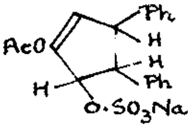


(VI)



(VII)

5 D. Vorlander and G. Schrödter, Ber., 1903, 36, 1490;

D. Vorlander and H.J. von Liebig, Ber., 1904, 37, 1133.

6 H.J. von Liebig, Annalen, 1914, 405, 188, 209.

7 G. Metge, Dissertation, Halle 1904.

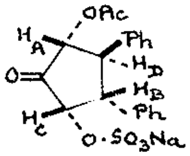
8 H. Burton and C.W. Shoppee, J. Chem. Soc., 1939, 567.

9 C.F.H. Allen, J.A. Van Allen, and J.F. Tinker, J. Org. Chem., 1955, 20, 1387.

Shoppee and Cooke (10) found that the sodium salt by heating with hydriodic acid and phosphorus gave a product shown by glc to contain four components: trans-1,2-diphenylcyclopentane (46%), its precursors 2,3-diphenylcyclopent-1-ene (16%) and 3,4-diphenylcyclopent-2-enone (29%), and cis-diphenylcyclopentane (0.1%); the two phenyl groups must therefore be trans to one another. The ^1H nmr spectrum of the sodium salt in dimethyl sulphoxide at 35° and 105°, recorded by Shoppee and Cooke (10) and given in Table 2, shows that formula (VII) is incorrect and must be replaced by the ketonic structure (VIII), which is consistent with all the chemical and physical data and was proved to be correct by Shoppee and Cooke (11) by the ^{13}C nmr proton-noise decoupled and off-resonance decoupled spectra in $[^2H_6]$-dimethyl sulphoxide.

Table 2

Proton	Ar	H_A	H_B	H_C	H_D	H_{Ac}
δ	7.2	5.85	3.9	3.5	3.2	2.0
	(10H,m)	(1H,q)	(1H,q)	(1H,dd)	(1H,dd)	(3H,s)
J/Hz	J_{AB} 0	J_{AC} 0.7	J_{AD} 12	J_{BC} 7	J_{BD} 11	J_{CD} 0

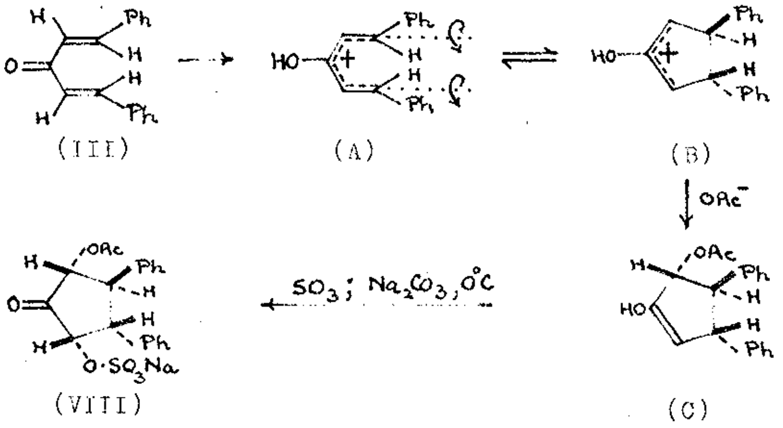


(VIII)

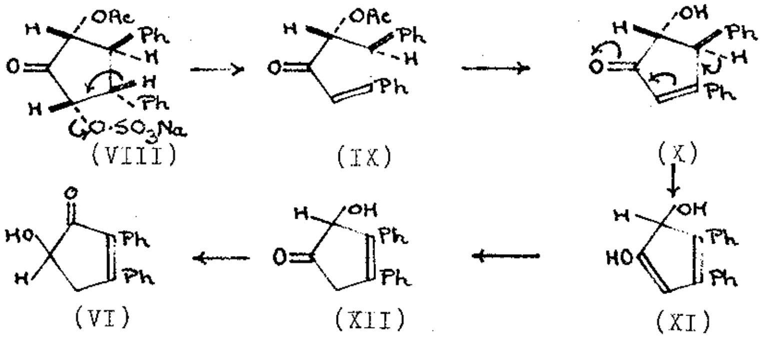
The mechanism of formation of the sodium salt (VIII) involves the conversion of trans-trans-dibenzylideneacetone (III) to the 1,5-diphenylpentadienyl cation (A), which undergoes a thermal conrotatory electrocyclic reaction to yield the diphenylcyclopentenyl cation (B); this, as the canonical form, coordinates with an acetate anion to give the enol (C), which undergoes sulphonation by sulphur trioxide (by a process analogous to that of the acid catalysed bromination of ketones) to afford, after quenching with aqueous sodium carbonate solution, the sodium salt (VIII).

10 C.W. Shoppee and B.J.A. Cooke, J. Chem. Soc. Perkin I, 1972, 2271.

11 C.W. Shoppee and B.J.A. Cooke, J. Chem. Soc. Perkin I, 1974, 189.



The perplexingly facile conversion of the sodium salt (VIII) by warm aqueous sodium carbonate solution into Vorlander's ketol (VI), sodium sulphite, and sodium acetate, is now readily explicable in terms of the β-elimination process (VIII → IX), with prior, concomitant, or subsequent ester hydrolysis of the acetate group (IX → X), followed by vinylogous enolisation (X → XI) and prototropy (XI → XII → VI).

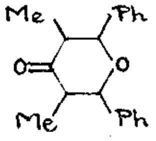


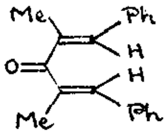
In 1904, Japp and Maitland (12) found that αα'-dimethyldibenzylideneacetone (XIV) with hot ethanolic hydrochloric acid or with hot hydriodic acid gave

12 F.R. Japp and W. Maitland, J. Chem. Soc., 1904, 85, 1473; cf. F.R. Japp and A.C. Michie, ibid., 1903, 83, 279.

2,5-dimethyl-3,4-diphenylcyclopent-2-enone (XV). Shoppee and Cooke (13) reinvestigated these reactions using modern techniques of analysis and identification. The primary product of the condensation of diethyl ketone and benzaldhyde with hydroxide ions is the tetrahydro-γ-pyrone (XIII) (14), which by the further action of hydroxide ions is converted into αα'-dimethyldibenzylideneacetone (XIV). Treatment of the pentadienone (XIV) with hot ethanolic hydrochloric acid gave a 78% yield of trans-4,5-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (XV). The same substance (XV) was obtained in small amount (4%) by use of hot hydriodic acid and red phosphorus together with much of a single isomer (one of six stereoisomers) (XVI) of 2,5-dimethyl-3,4-diphenylcyclopentanone (64%). Japp and Maitland (12) described the conversion of the tetrahydro-γ-pyrone (XIII) by hot hydriodic acid to a mixture (ca. 3:1) of the cyclopentenanone (XV) and the cyclopentanone (XVI); Shoppee and Cooke (13) found that the cyclopentenone (XV) is only partly reduced by hydriodic acid to the cyclopentanone (XVI).

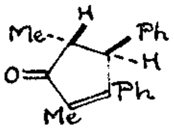
(XIII)

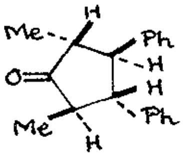




(XIV)

(XV)





(XVI)

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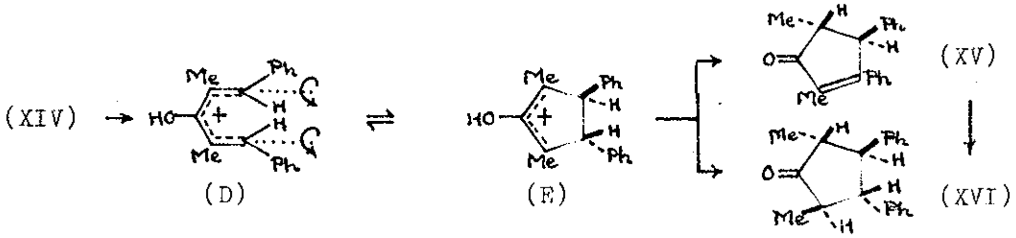
13 C.W. Shoppee and B.J.A. Cooke, J. Chem. Soc. Perkin I, 1973, 1026.

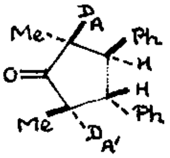
14 D. Vorlander and K. Hobohm, Ber., 1896, 29, 1352, 1836; cf. D. Vorlander and F. Wilcke, ibid., 1898, 31, 187.

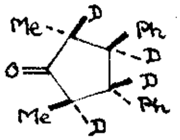
The formation from the pentadienone (XIV) of the cyclopentenone (XV) and the cyclopentanone (XVI), whose configurations are those consistent with thermodynamic control, occurs by a thermal ground state conrotatory electrocyclic reaction. In general, symmetry allowed electrocyclic reactions are subject to thermodynamic control. The pentadienone (XIV) by protonation yields the pentadienyl cation (D), cyclised to the cyclopentenyl cation (E), which in the presence of hydrogen chloride can eliminate a benzylic proton to furnish the cyclopentenone (XV) with partial loss of stereochemistry, or in the presence of hydrogen iodide can undergo reduction to the cyclopentanone (XVI). However, since the cyclopentenone (XV) is partly reduced by hydrogen iodide to the cyclopentanone (XVI), the stereochemistry of the latter may not reflect the geometry of the cyclisation.



Shoppee and Cooke (13) used deuterium iodide to distinguish between the two pathways (E → XVI) and (E → XV → XVI); the former pathway leads to the presence of two benzylic protons (XVII) and the latter pathway to the incorporation of benzylic deuterons (XVIII).

(XVII)

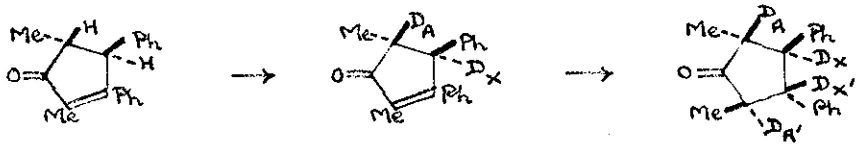




(XVIII)

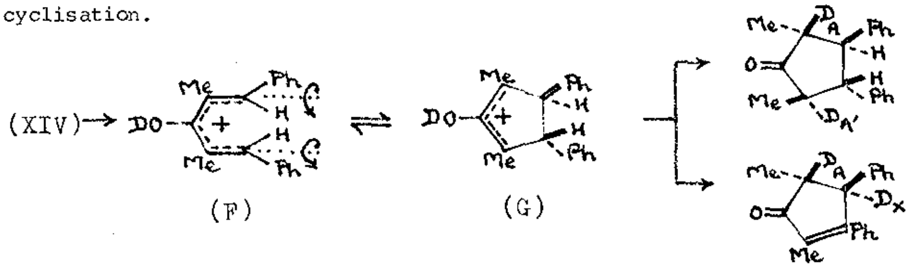
The cyclopentenone (XV) with deuterium iodide (isotopic purity 99%) and red phosphorus at 60-65°C for 24 hours gave the isomer (XIX; D_A 82%, D_X 84%) by exchange but suffered very little reduction to the cyclopentanone (XVIII). The pentadienone (XIV) with deuterium iodide and red phosphorus at 60-65°C for

18 hours gave the cyclopentenone (XIX; $D_A = D_X$ 80%) together with an amount of a cyclopentanone (XVII?) too small to permit determination of the isotopic distribution. In a similar experiment at 90-95°C for 18 hours, the pentadienone (XIV) gave the cyclopentenone (XIX; $D_A = D_X$ 80%) and the cyclopentanone (XVIII; $D_A = D_{A'}$ 80%, $D_X = D_{X'}$ 67%) in the proportion of 28:72. The limiting degree of deuteration producible by deuterium iodide reduction of the cyclopentenone (XIX; D_A 80%, D_X 80%) should be represented by the cyclopentanone (XVIII; $D_A = D_X$ 80%, $D_{A'} = D_{X'}$ 99%) which would be indistinguishable by nmr spectroscopy from (XVIII; $D_A = D_X = D_{A'} = D_{X'}$ 90%). If the exchange of methine and benzylic protons (XV → XIX) is 80% complete (a low estimate in view of the exchange data described above) before reduction (XIX → XVIII) occurs to an appreciable extent, it follows that up to 23% of the cyclisation product of the pentadienone (XIV) with deuterium iodide has the structure (XVII; $D_A = D_{A'}$ 80%) containing two benzylic protons.



(XV) (XIX) (XVIII)

Up to 23% of the pentadienone (XIV) is thus converted with deuterium iodide into the cyclopentanone (XVII) by a conrotatory ground state electrocyclic reaction (XIV → F → G → XVII) with preservation of the stereochemistry of cyclisation.

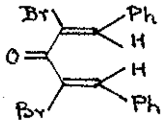


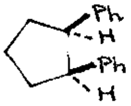
(F) (G) (XVII) (XIX)

This conclusion may reasonably be extended to the conrotatory ground state electrocyclic reaction sequence with hydrogen iodide (XIV → D → E → XVI).

In 1914, Hellthaler (15) reported that αα'-dibromodibenzylideneacetone (XX) by reduction with hot hydriodic acid and red phosphorus gave a 60% yield of cis-1,2-diphenylcyclopentane (XXI). The dibromoketone (XX) has recently been shown by Alcock and Sawyer (at the writer's suggestion) (16) by X-ray crystallography to have the trans-trans(H/Br)-configuration depicted. Conversion of the derived cation into a precursor of cis-1,2-diphenylcyclopentane (XXI) would involve a thermally forbidden disrotatory electrocyclic reaction and would violate the selection rules (Table 1) for conservation of orbital symmetry in a concerted reaction.

(XX)





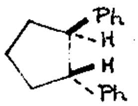
(XXI)

Shoppee and Cooke (17) re-examined the reaction of the dibromoketone (XX) with hydriodic acid under Hellthaler's conditions. The product was a complex mixture of cyclic compounds (68%) together with a polymeric hydrocarbon (25%). Analysis by column chromatography followed by glc disclosed the presence of cis-1,2-diphenylcyclopentane (XXI; 11%), trans-1,2-diphenylcyclopentane (XXII; 29%), 3,4-diphenylcyclopent-2-enone (XXIII; 11%), and trans-3,4-diphenylcyclopentanone (IV; 17%). It was shown that the cyclopentenone (XXIII) is not reduced to the cyclopentanone (IV) under the conditions employed, and it was known (10) that the cyclopentanone (IV) is also not reduced to trans-1,2-diphenylcyclopentane (XXII) under the conditions used.

15 G. Hellthaler, Annalen, 1914, 406, 161.

16 N.W. Alcock and J.F. Sawyer, Acta Cryst., 1976, B 32, 285.

17 C.W. Shoppee and B.J.A. Cooke, J. Chem. Soc. Perkin I, 1973, 2197.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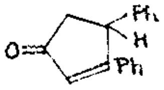
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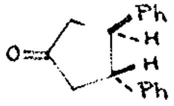
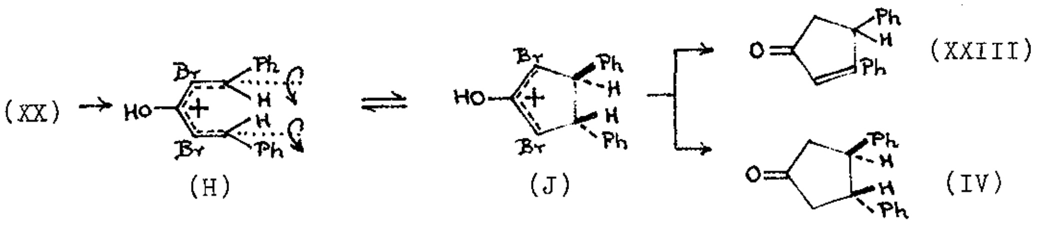
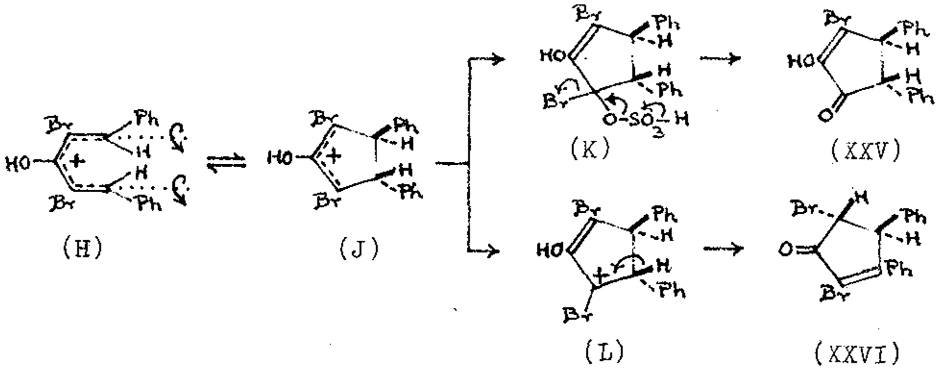

(IV)

Reduction of the cyclopentenone (XXIII) appears to be responsible for the formation of both the cis-hydrocarbon (XXI) and the trans-hydrocarbon (XXII) in the cyclisation of the dibromopentadienone (XX). It is thus possible to account for the production of the cis-hydrocarbon (XXI) reported by Hellthaler (15) but not for his claimed 60% yield of crude compound. Hellthaler's product *was isolated by steam distillation of the reaction mixture* (both the cis- and trans-hydrocarbons are volatile in steam), crystallisation of the solidified distillation material from acetone-ethanol-water with possible loss of any trans-hydrocarbon (XXII); presumably any cyclopentenone (XXIII) and cyclopentanone (IV) formed in the reaction remained in the steam-involatile residue which was not further examined.

The dibromopentadienone (XX) as the pentadienyl cation (H) undergoes a thermal ground state conrotatory electrocyclic reaction to yield the cyclopentenyl cation (J), which by elimination of a benzylic proton and reductive removal of both bromine atoms affords 3,4-diphenylcyclopent-2-enone (XXIII), or furnishes directly by reduction trans-3,4-diphenylcyclopentanone (IV) which retains and reveals the stereochemistry of the cyclisation process.



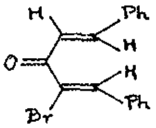
Shoppee and Cooke (17) also investigated the action of conc. sulphuric acid at 25° on the dibromopentadienone (XX), and observed nearly quantitative conversion to the quasi-acidic 3-bromo-2-hydroxy-*trans*-4,5-diphenylcyclopent-2-enone (XXV; 10%) and the neutral yellow *trans*-2,5-dibromo-3,4-diphenylcyclopent-2-enone (XXVI; 85%). The dibromopentadienyl cation (H) again undergoes a thermal ground state conrotatory electrocyclic reaction to give the dibromocyclopentenyl cation (J). This either coordinates with a bisulphate anion to furnish the hydrogen sulphate (K) which eliminates hydrogen bromide and sulphur trioxide by a concerted process to afford the unsaturated bromohydroxyketone (XXV), or as the canonical form (L) loses a benzylic proton to yield the unsaturated dibromoketone (XXVI).

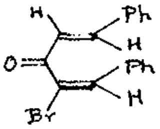


The nearly quantitative yield of the cyclic products is due to the irreversibility of the cyclisation process (H → J≡L) caused by elimination of hydrogen bromide (K → XXV) and by depolarisation of the carbonium ion by loss of a proton (L → XXVI).

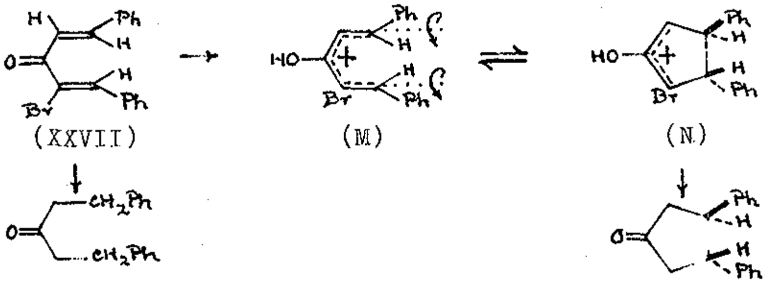
Shoppee and Cooke (18) also examined the reactions of α-bromodibenzylideneacetone, which constitutes a stereoelectronic case intermediate between dibenzylideneacetone (III) and αα'-dibromodibenzylideneacetone (XX), with hydriodic acid and conc. sulphuric acid. The monobromoketone exists as the *trans*-*trans*-isomer (XXVII) (15) and the *cis*-*trans*-isomer (XXVIII) (18); the latter is readily rearranged to the former by a catalytic trace of iodine.

18 C.W. Shoppee and B.J.A. Cooke, *J. Chem. Soc. Perkin I*, 1975, 2210.

(XXVII) 

 (XXVIII)

The trans-trans-isomer (XXVII) with hot hydriodic acid-acetic acid (1:9) and a little red phosphorus gave by reduction 1,5-diphenylpentan-3-one (XXIX; 20%) and by a thermal symmetry allowed conrotatory electrocyclic reaction (M → N) and reductive removal of the bromine atom trans-3,4-diphenylcyclopentanone (IV; 57%). The cis-trans-isomer (XXVIII) furnished the same products (10% and 52% respectively) but failed to give the expected cyclic product cis-3,4-diphenylcyclopentanone (8, 19); conversion of the cis-trans-isomer (XXVIII) to the trans-trans-isomer (XXVII) clearly precedes cyclisation.



(XXVII) (M) (N)

(XXIX) (IV)

With conc. sulphuric acid at 0° the trans-trans-isomer (XXVII) was little changed, but at 25° gave 2-bromo-3,4-diphenylcyclopent-2-enone (XXX; 40%), the isomeric trans-2-bromo-3,4-diphenylcyclopent-4-enone (XXXI; 18%), and Vorlander's ketol (VI; 1%). A 92% pure sample of the cis-trans-isomer (XXVIII) reacted readily with conc. sulphuric acid at 0° to give the trans-trans-isomer (XXVII; 6% of the 8% present in the starting material), the three compounds (XXX; 23%), (XXXI; 13%),

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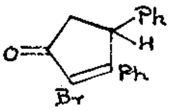
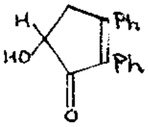
19 H.A. Weidlich, Ber., 1938, 71, 1601; H.A. Weidlich and M. Meyer-Delius, ibid., 1941, 74, 1195.

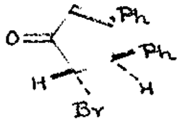
(VI; 2%), the dienone (XXXII; 8%) as the known dimer (XXXIII) (20, 21), and the labile cis-2-bromo-3,4-diphenylcyclopent-4-enone (XXXIV; 38%).



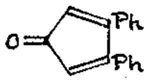
(XXX)



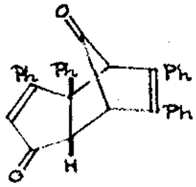
(VI)



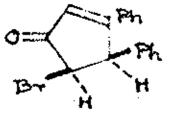
(XXXI)



(XXXII)



(XXXIII)

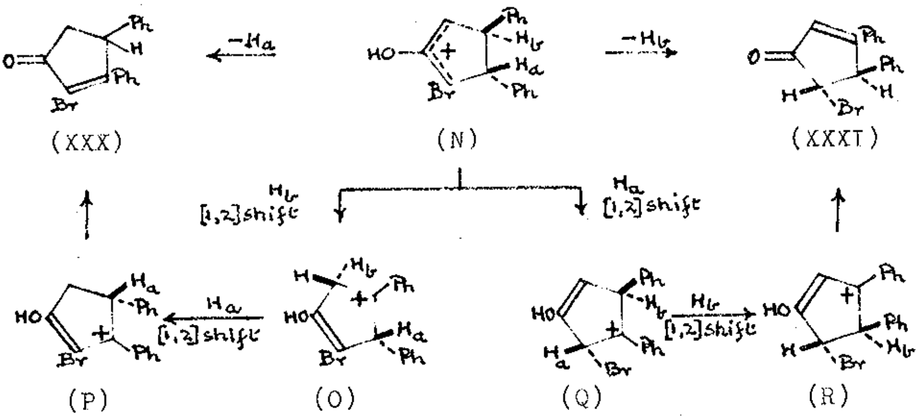


(XXXIV)

The trans-trans-isomer (XXVII) undergoes a thermal conrotatory electrocyclic reaction (M → N). The cyclopentenyl cation (N) can lose a benzylic proton to yield, after ketonisation, either of the bromoketones (XXX), (XXXI) or combine with the hydrogen sulphate anion to give by concerted loss of hydrogen bromide and sulphur trioxide, followed by prototropy, Vorländer's ketol (VI), but can also undergo a sequence of two suprafacial [1,2]sigmatropic shifts to afford the carbonium ions (O and P) or (Q and R) which lead to bromoketones (XXX) and (XXXI) respectively.

20 P. Bladon, S. McVey, P.L. Paulson, G.D. Broadhead, and W.M. Horspool, J. Chem. Soc. (C), 1966, 306.

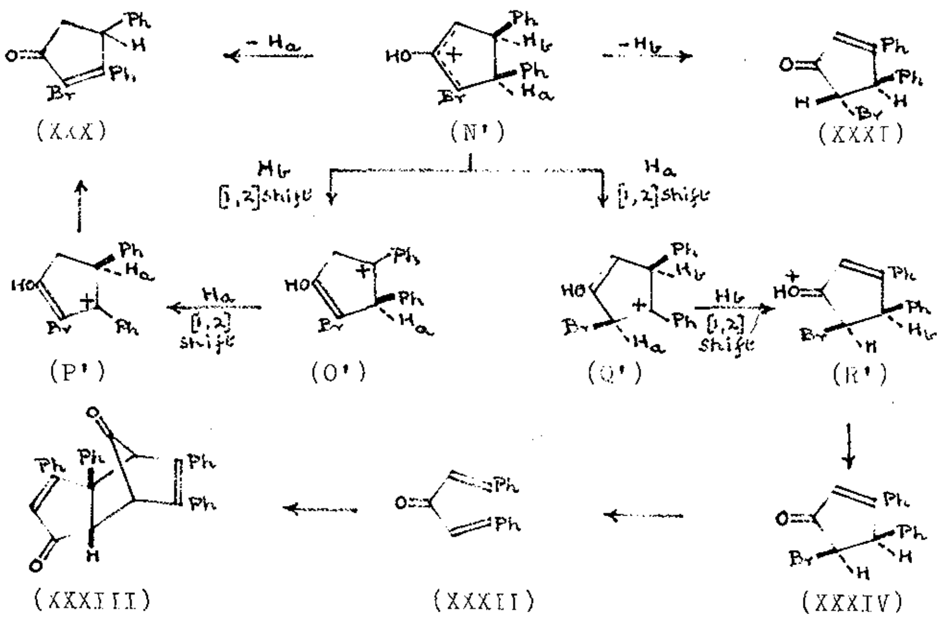
21 B. Fuchs, J. Amer. Chem. Soc., 1971, 93, 2544.



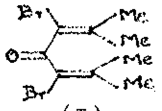
The two pathways delineated above cannot be distinguished in the absence of data from suitably labelled substrates.

In the case of the cis-trans-isomer (XXVIII), the formation and properties of the bromoketone (XXXIV) enable the two pathways to be distinguished. The bromoketone (XXXIV) with cold dilute sodium hydroxide gives, by enolisation and inversion of configuration, the isomer (XXXI; 67%), and by trans-dehydrobromoation the dienone (XXXII; 33%) as the dimer (XXXIII); analysis of the yield data shows that the eliminative pathway accounts for <10% and the sigmatropic shift pathway for >90% of the products.

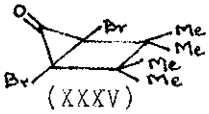
The cis-trans-isomer (XXVIII) undergoes a thermal conrotatory electrocyclic reaction (M' → N'). The cation (N') (10%) loses a benzylic proton in two ways to give the bromoketones (XXX) and (XXXI); or the cation (N') (90%) undergoes a sequence of two suprafacial sigmatropic shifts, which relieve the steric strain caused by the eclipsed phenyl groups, to furnish the carbonium ions (Q' and R') and (O' and P'). Carbonium ion (R') by deprotonation gives the bromoketone (XXXIV), trans-dehydrobrominated to the dienone (XXXII) and its dimer (XXXIII); carbonium ion (P') by deprotonation can give only the bromoketone (XXX).



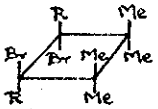
Shoppee and Wang (22) explored the photochemistry of αα'-dibromophorone (I). A photochemical excited state disrotatory electrocyclic reaction is symmetry allowed (Table 1), and could lead to a bicyclo[2,1,0]pentanone (XXXV) by internal coupling of the two ethylenic centres or to a series of cyclobutane dimers (XXXVI - XXXIX) by concerted external coupling of two excited molecules.



(I)

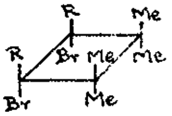


(XXXV)



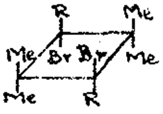
(XXXVI)

(Head/head,staggered)



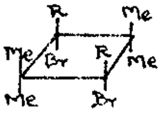
(XXXVII)

(Head/head,eclipsed)



(XXXVIII)

(Head/tail)



(XXXIX)

(Head/tail)

(R = $Me_2C{=}CBr{-}CO{-}$)

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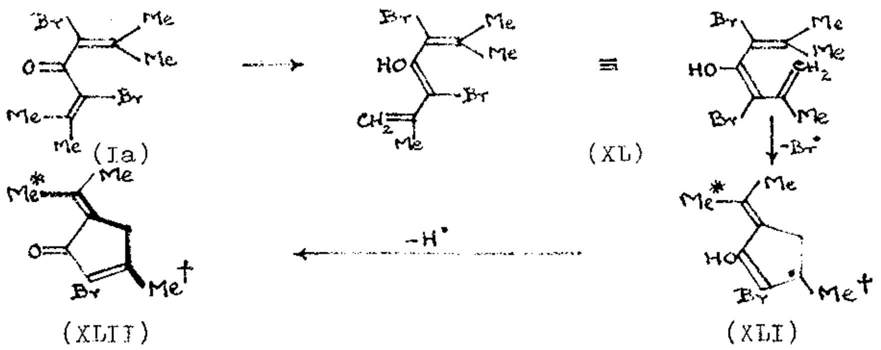
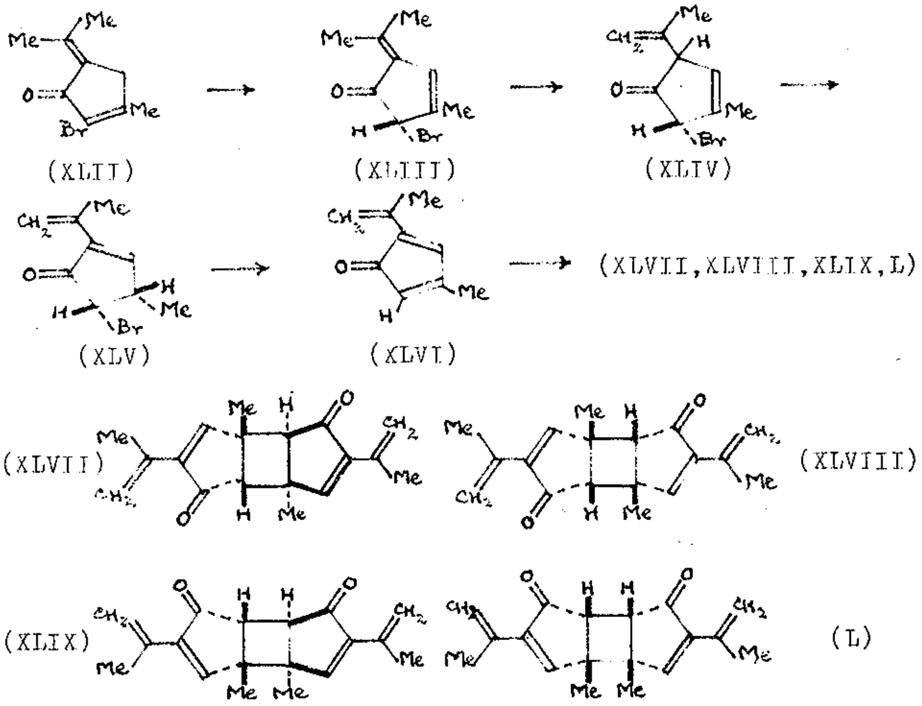
22 C.W. Shoppee and Y-S. Wang, J. Chem. Soc. Perkin I, 1975, 1595.

The dibromodienone (I) by irradiation in hexane under nitrogen at ca. 300 nm failed to yield a compound of type (XXXV) or any of the cyclobutane dimers (XXXVI - XXXIX); the major photoproduct was 2-bromo-5-isopropylidene-3-methylcyclopent-2-enone (XLII). It appears to arise from the s-cis-trans-conformation (Ia) of the dibromodienone (I) by hydrogen abstraction to yield the photoenol (XL), which is cyclised by photochemical loss of a bromine atom to give the intermediate (XLI), transformed into the photoproduct (XLII). The ^{1}H nmr spectrum of the cyclopentenone (XLII) exhibits a remarkable long-range



coupling of "W"-type between the protons of the methyl groups Me^{*} and $Me^{\dagger}$ (J 0.3 Hz) across seven bonds.

The minor photoproduct was a derivative of tricyclo$[5,3,0,0^{2,6}]$decane possessing one of the four isomeric structures (XLVII - L). It arises from the major photoproduct (XLII) by a series of $\alpha\beta$-$\beta\gamma$ changes giving a sequence of isomers (XLIII - XLV), the last of which (XLV) by loss of hydrogen bromide furnishes the cyclopentadienone (XLVI). This can dimerise by a symmetry allowed excited state cycloaddition in four ways: (i) head-to-tail, staggered → (XLVII); (ii) head-to-tail, eclipsed → (XLVIII); (iii) head-to-head, staggered → (XLIX); (iv) head-to-head eclipsed → (L). The ^{1}H nmr spectrum is consistent with the structure (XLVII), eliminates structure (XLVIII), but does not exclude structures (XLIX) and (L).



(XLII) (XLIII) (XLIV)

(XLV) (XLVI) (XLVII,XLVIII,XLIX,L)

(XLVII) (XLVIII)

(XLIX) (L)

In 1909, Ciamician and Silber (23) found that yellow trans-trans-dibenzylideneacetone (III) in ethanol by irradiation with summer sunshine in Bologna yielded a colourless dimer. Some 45 years later this dimer was obtained pure by Pitts *et al.*, (24), and shown to be of truxinic type by oxidation with boiling aqueous potassium permanganate to δ-truxinic acid; owing to the possibility of inversion of configuration at a carbon atom α to a carboxyl group by prototropy in the oxidation product, an unequivocal assignment of structure to the dimer was not made. Shoppee *et al.*, (25) by irradiation of the dienone (III) in hexane

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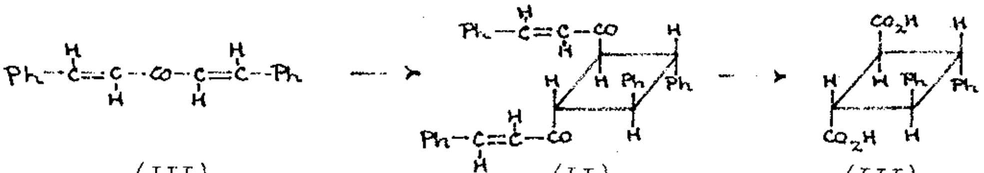
23 G. Ciamician and P. Silber, Ber. 1909, 42, 1386.

24 G.W. Rechtenwald, J.N. Pitts Jr., and R.L. Letsinger, J. Amer. Chem. Soc., 1953, 75, 3028.

25 C.W. Shoppee, Y-S. Wang, S. Sternhell, and G.C. Brophy, J. Chem. Soc. Perkin I, 1976 in the press.

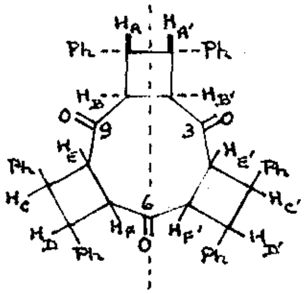
in nitrogen at ca. 300 nm or in *iso*propanol-benzene at λ 280-360 nm under nitrogen obtained the dimer as the major photoproduct, and showed it to have the all-*trans* structure (LI) by oxidation with chromium trioxide-acetic acid to δ-truxinic acid (LII) and by its ^{1}H and ^{13}C nmr spectra. The dimer is formed by a concerted photochemical symmetry allowed cycloaddition of two head-to-head staggered excited molecules of the dienone (III).

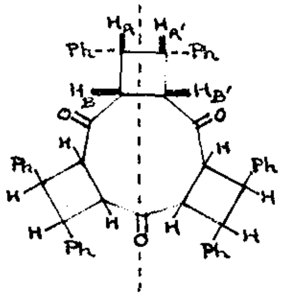


(III) (LI) (LII)

Four stereoisomeric trimers were isolated as minor photoproducts and shown by ^{1}H nmr spectroscopy and mass spectrometry to be derivatives of tri(cyclobuta)[a,d,g]nonane-3,6,9-trione. The ^{1}H nmr spectral data for one trimer show conclusively *that it has the gross structure (LIII) or (LIV)*, possessing the plane of symmetry shown, with the "unique" cyclobutane ring (AA'BB') having either *cis*/*trans*/*cis*-geometry (LIII) or *cis*/*cis*/*cis*-geometry (LIV). The small size of the long-range coupling constant in the unique cyclobutane ring J_{AB}, -0.18 Hz suggests a *trans*-relationship between H_A and H_B, thus making structure (LIII) more probable than (LIV). Similarly, the small value of J_{CF} -0.69 suggests that H_C and H_F are probably *trans*-orientated, but this is insufficient for a complete description of the stereochemistry of (LIII) or (LIV).

(LIII)

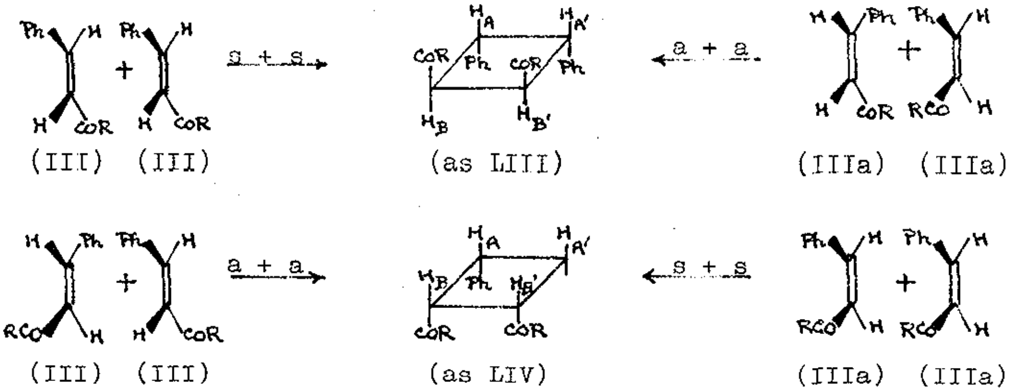




(LIV)

A second cyclic trimer possesses a ^{1}H nmr spectrum which shows that the molecule lacks any symmetry, so that the twelve hydrogen atoms in the three cyclobutane rings all have different environments. Various structures analogous to (LIII) complying with this requirement can be devised, but there is no evidence to identify any one of them with this trimer. Similarly, the ^{1}H nmr and mass spectra of a third and a fourth trimer are consistent with structures analogous to (LIII) but do not specify the stereochemistry.

The photochemical formation of the unique cyclobutane ring of the trimer (LIII) requires, as the initial step (i) head-to-head $[_{\pi}2_s + _{\pi}2_s]$ cycloaddiation of two eclipsed excited molecules of trans-trans-dibenzylideneacetone (III), or (ii) photochemical conversion of (III) to the cis-trans-isomer (IIIa) followed by head-to head $[_{\pi}2_a + _{\pi}2_a]$ cycloaddition of two staggered excited molecules.



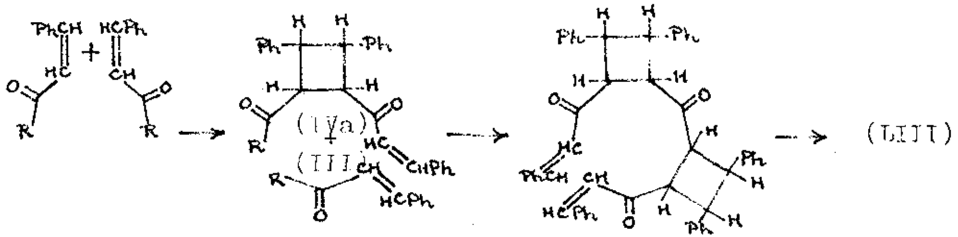
(III) (III) (as LIII) (IIIa) (IIIa)

(III) (III) (as LIV) (IIIa) (IIIa)

(R = PhCH=CH-)

Similarly, the photochemical formation of the unique cyclobutane ring of the trimer (LIV) requires as the initial step (i) head-to-head $[_{\pi}2_a + _{\pi}2_a]$ cycloaddition of two staggered excited molecules of trans-trans-dibenzylideneacetone (III), or head-to-head $[_{\pi}2_s + _{\pi}2_s]$ cycloaddition of two eclipsed excited molecules of photochemically generated cis-trans-dibenzylideneacetone (IIIa).

A mechanism for the photochemical formation of cyclic trimers of type (LIII) encounters serious difficulties on account of entropy factors. However, three consecutive photochemical $[{}_{\pi}2_{s} + {}_{\pi}2_{s}]$ or $[{}_{\pi}2_{a} + {}_{\pi}2_{a}]$ cycloadditions could lead to stereoisomeric structures of the required type [(III) + (III) → (IVa) + (III) → (LV) → (LIII)]. Alternatively and more simply, and therefore more probably, a bimolecular photochemical $[{}_{\pi}2_{s} + {}_{\pi}2_{s}]$ or $[{}_{\pi}2_{a} + {}_{\pi}2_{a}]$ cycloaddition of the photodimer (IVa) to the monomer (III) could also lead to trimeric structures of the required type [(IVa) + (III) → (LV) → (LIII)].

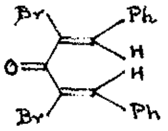


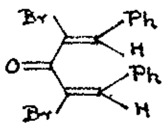
(III) (III) (LV)

trans-trans-αα'-Dibromodibenzylideneacetone (XX), unlike trans-trans-αα'-dibromophorone(I), is structurally incapable of undergoing deconjugation and of yielding derivatives of cyclopentane (cf. XLII) by loss of hydrogen bromide. Shoppee and Wang (26) however found that impact of photons or electrons on the dibromodienone (XX) leads to elimination of hydrogen bromide, which may be followed by dimerisation; alternatively, photochemical dimerisation may be succeeded by loss of hydrogen bromide.

Irradiation of the dibromodienone, $C_{17}H_{12}Br_{2}O$, (XX) in toluene or in benzene-isopropanol under nitrogen at ca. 300 nm afforded the yellow cis-trans-isomer (XXa) and four colourless cyclic products.

(XX)





(XXa)

One photoproduct, $C_{17}H_{11}BrO$, can arise by transformation of the trans-trans-isomer (XX) to the cis-trans-isomer (XXa), which in the s-cis-trans-conformation

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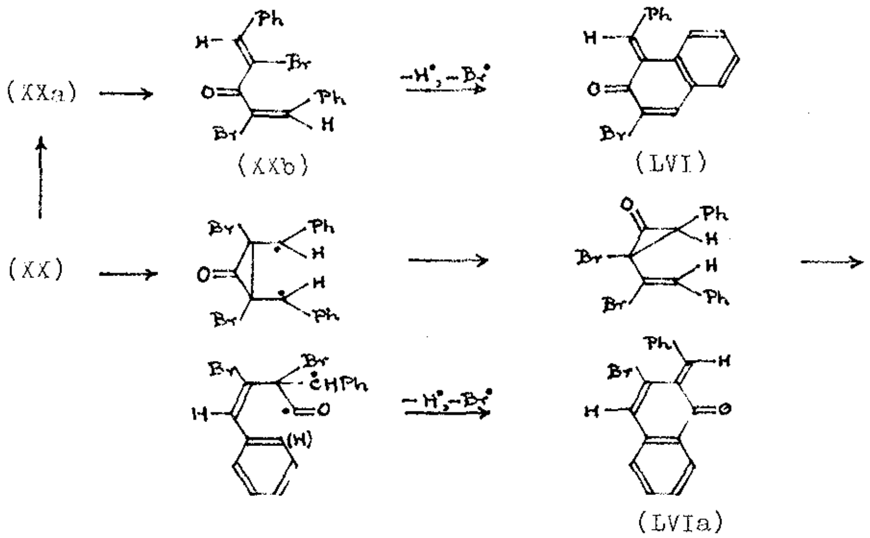
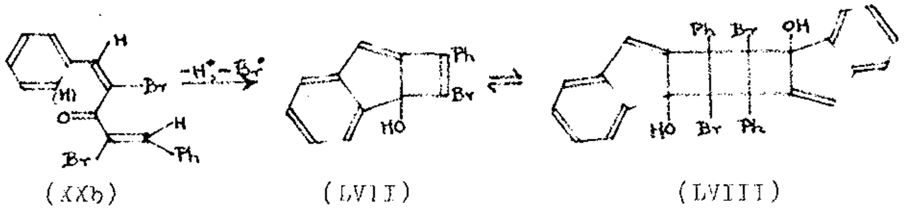
26 C.W. Shoppee and Y-S. Wang, J. Chem. Soc. Perkin I, 1976, in the press.

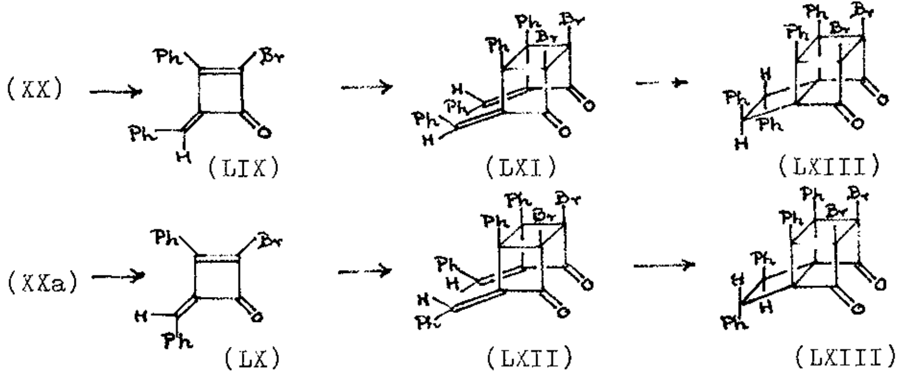
(XXb) loses an ortho-hydrogen atom as hydrogen bromide giving the naphthalenone (LVl). There is an alternative formula (LVIa), which is not excluded by the structural evidence and which could be produced by a di-π-oxomethane rearrangement of the s-trans-trans-conformation of the dibromodienone (XX).



A second photoproduct, $C_{34}H_{22}Br_2O_2$, contained a hydroxyl group but no carbonyl group. The ^{1}H nmr spectrum integrated for 22 protons, but the mass spectrum showed no cluster of peaks at m/e 624, 622, 620; instead a pair of intense isotopic peaks were seen at m/e 312, 310 (1:1), and a pair of even more intense peaks at m/e 311, 309 (1:1) suggesting the presence of a labile hydrogen atom. The structural evidence is consistent only with a fragile dimer, which by electron impact (or thermally) breaks up to give the monomer. The cis-trans-dibromodienone (XXa) in the s-cis-trans-conformation (XXb) can undergo a photochemical intramolecular reduction with prior or subsequent elimination of hydrogen bromide to yield the monomeric bromohydroxycyclobutaindene (LVII), which then affords the symmetrical dimer (LVIII).

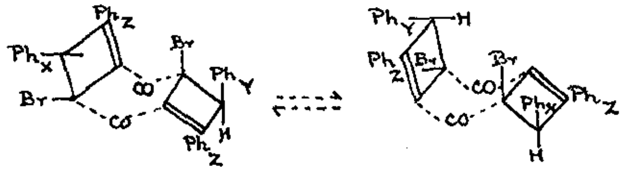


The major photoproduct, $C_{34}H_{22}Br_2O_2$, gave a remarkably simple ^1H nmr spectrum containing only two one-proton AB-doublets and two multiplets for 16 aromatic protons and 4 aromatic protons respectively, so that there are present two pairs of phenyl groups with the four ortho-protons of one pair in a different environment from the four ortho-protons of the other pair. These observations lead to the secocubanedione structure (LXIII), which is supported by the ir spectrum with two carbonyl stretching frequencies (ν 1790, 1705 cm^{-1}) and by the mass spectral fragmentation pattern with alternate and duplicate loss of carbon monoxide and bromine. The d- and l-forms of the dibromotetraphenylpentacyclo $[4.2.2.0^{1,6},0^{3,8},0^{4,7}]$decane-2,5-dione (LXIII) are derived from the trans-trans-(XX) and cis-trans-dibromodienone (XXa) by elimination of hydrogen bromide to give the isomeric bromo-phenylcyclobutenones (LIX, LX), which respectively undergo a photochemical symmetry allowed $[_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition to furnish the intermediates (LXI, LXII), which by further absorption of photons undergo subsequent symmetry allowed $[_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition of the two staggered benzylidene side-chains.



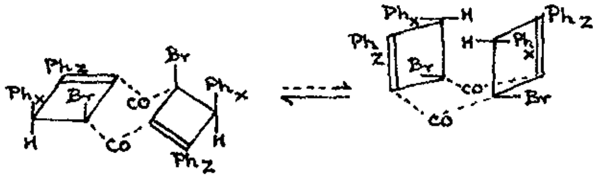
The other major photoproduct, also $C_{34}H_{22}Br_2O_2$, exhibited a single carbonyl maximum at 1720 cm^{-1}; both carbonyl groups must therefore possess similar environments, whilst the mass spectral fragmentation pattern showed that they must be cyclic with alternate and duplicate loss of carbon monoxide, bromine, and hydrogen bromide. The ^1H nmr spectrum was illuminating and exhibited two uncoupled one-proton singlets and three multiplets for 16 aromatic protons, 2 aromatic protons, and 2 aromatic protons respectively, so that there are present three different types of phenyl group. These observations are consistent with the dibromotetraphenyltricyclo[6,2,0,$0^{3,6}$]decane-2,7-dione structure LXVI), which can exist in two anti-conformations (LXVIa and b), and exclude the two theoretically possible syn-conformations (LXVIIa and b). There was no interconversion of the conformers (LXVIa and b) up to 110°C in deuteriochloroform since the two one-proton singlet signals in the ^1H nmr spectrum remained unchanged.

(LXVIa)



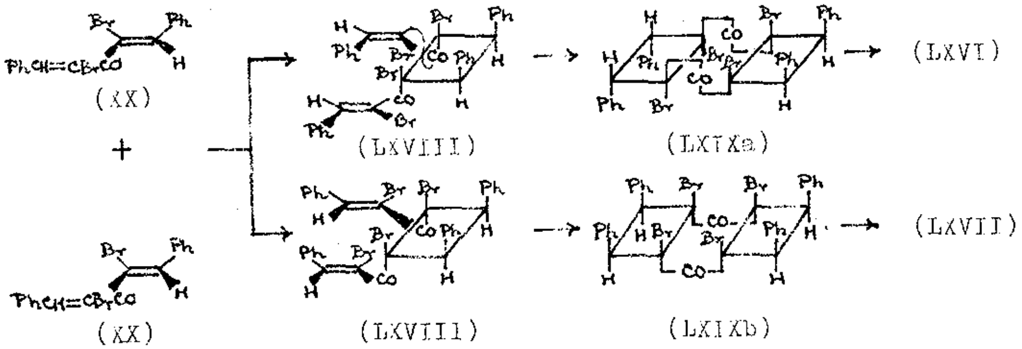
(LXVIb)

(LXVIIa)

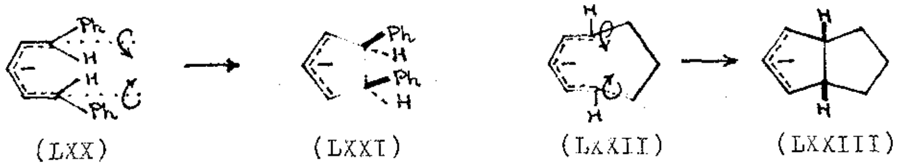


(LXVIIb)

Formation of the tricyclic structures (LXVI) and (LXVII) requires that two head-to-head eclipsed molecules of αα'-dibromodibenzylideneacetone (XX) undergo a photochemical symmetry allowed [$_{\pi}2_s + _{\pi}2_s$] cycloaddition to give (LXVIII) possessing cis-1,2-α-bromobenzylidene side-chains. Absorption of photons by (LXVIII) then leads to a second symmetry allowed [$_{\pi}2_s + _{\pi}2_s$] cycloaddition to furnish the intermediates (LXIXa) and (LXIXb), which by symmetrical photochemical trans-elimination of two molecules of hydrogen bromide afford the anti-dl-pair represented by (LXVI) or the syn-dl-pair represented by (LXVII).



In 1975, Shoppee and Henderson (27) described the thermal six-electron $[{}_{\pi}2_s + {}_{\omega}2_s + {}_{\pi}2_s]$ disrotatory electrocyclisation (cf. Table 1) of the 1,5-diphenylpentadienide anion (LXX) to the cis-4,5-diphenylcyclopentenide anion (LXXI). The sole previous example of such a transformation was the thermal disrotatory conversion in 1967 by Bates and McCombs (28) of the cyclooactadienide ion (LXXII) to the cis-bicyclo[3,3,0]octenide ion (LXXIII).



Generation of the anion (LXX) from trans-trans-1,5-diphenylpentadiene with sodamide or n-butyllithium in diglyme or in decalin and heating at 160° or at 190° for extended periods failed, after quenching, to yield cis-3,4-diphenylcyclopentene (LXXIV) and gave intractable polymers of unknown structure. However, generation of the anion (LXX) in situ from dibenzylideneacetone semicarbazone with powdered potassium t-butoxide at 225° using the Wolff-Kishner reaction:

$$NH_2CO\text{-}NH\text{-}N{=}< \rightarrow \bar{N}H\text{-}N\text{-}CH< \rightarrow N_2 + \bar{C}H<$$

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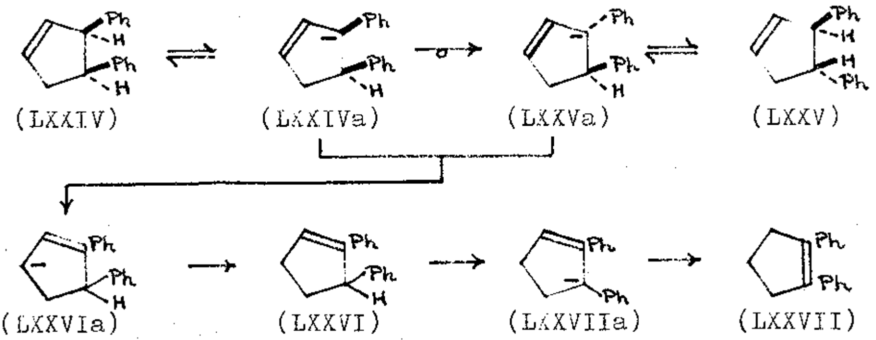
27 C.W. Shoppee and G.N. Henderson, J. Chem. Soc. Perkin I, 1975, 765.

28 R.B. Bates and D.A. McCombs, Tetrahedron Letters, 1967, 977.

gave a mixture of *cis*-3,4-diphenylcyclopentene (LXXIV), *trans*-3,4-diphenylcyclopentene (LXXV), and the conjugated isomers (LXXVI) and (LXXVII). *cis*-3,4-Diphenylcyclopentene (LXXIV) may be the sole initial cyclisation product since with powdered potassium *t*-butoxide at 225°C both the *cis*- and *trans*-isomers (LXXIV) and (LXXV) undergo conversion to the conjugated isomers (LXXVI) and (LXXVII), a change presumably involving the anions (LXXIVa), (LXXVa), (LXXVIa) and (LXVIIa).



Shoppee and Henderson (29) generated the anion (LXX) from the *p*-toluenesulphonylhydrazone (LXXVIII), depicted in the s-*cis*-*trans*-conformation, of *trans*-*trans*-dibenzylideneacetone (III) with lithium aluminium hydride in ether at 35°C or in tetrahydrofuran at 65°C by the Caglioti reaction (30):

$$\text{Ts-NH-N=C<} \rightarrow \text{Ts-}\bar{\text{N}}\text{-N=C<} \rightarrow \bar{\text{N}}\text{=N-CH<} \rightarrow \text{N}_2 + \bar{\text{C}}\text{H<},$$

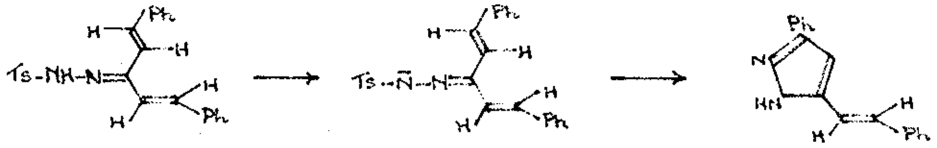
or by use of *n*-butyllithium in ether, and from 3-methoxy-1,5-diphenylpenta-1,4-diene with sodium-potassium alloy in tetrahydrofuran at 0° by the classical method of Ziegler and Schnell (31). All these methods failed* to yield *cis*-3,4-diphenylcyclopentene (LXXIV), and gave the reduction products *cis*- or *trans*-1,5 diphenylpentene together with unidentified substances. The sulphonylhydrazone (LXXVIII) by thermal treatment with methoxide ions in methanol gave the anion

29 C.W. Shoppee and G.N. Henderson, *J. Chem. Soc. Perkin I*, 1976 in the press.

30 L. Caglioti, *Tetrahedron*, 1963, *19*, 1127; 1967, *22*, 487.

31 K. Ziegler and B. Schnell, *Annalen*, 1924, *437*, 227.

(LXXVIIIa), which cyclised to afford the known 3(5)-phenyl-5(3)-styrylpyrazole (LXXIX), which was also produced by irradiation of the sulphonylhydrazone (LXXVIII) at ca. 300 nm in methanol under nitrogen.



(LXXVIII) (LXXVIIIa) (LXXIX)

The writer acknowledges the support of the Welch Foundation, Houston, Texas, U.S.A. and the work of Dr. B.J.A. Cooke, Dr. G.N. Henderson, Dr. Y-S. Wang (whilst Welch Postdoctoral Research Fellows), and his former colleagues Dr. R.E. Gall (née Lack), Dr. S. Sternhell, and Mr. G.C. Brophy of the University of Sydney.

* The Caglioti reaction has now been found to yield the anion (LXXI) of cis-3,4-diphenylcyclopentene, isolated as (LXXVI).

Received, 15th June, 1976