

Electrocyclic Reactions. Part IX.¹ Photolysis of *trans,trans*-2,4-Dibromo-1,5-diphenylpenta-1,4-dien-3-one ($\alpha\alpha'$ -Dibromodibenzylideneacetone)

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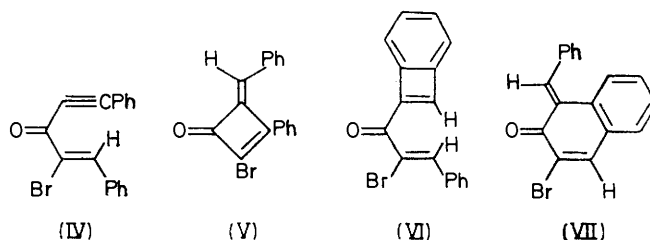
Irradiation of *trans,trans*- $\alpha\alpha'$ -dibromodibenzylideneacetone (I) in benzene-propan-2-ol or toluene at 30 °C under nitrogen at 300 nm yielded a little of the *cis,trans*-isomer (II) and, by loss of hydrogen bromide, one bicyclic product $C_{17}H_{11}BrO$ and three polycyclic products $(C_{17}H_{11}BrO)_2$. The former is a 1-benzylidenenaphthalen-2-one derivative (VIIa): one of the latter is regarded as a pentacyclo[4.2.2.0^{1,6}.0^{3,8}.0^{4,7}]decane-2,5-dione derivative (X), and another is considered to be a tricyclo[6.2.0.0^{3,6}]decane-2,7-dione derivative (XVIIIa or b). The evidence for the structures of these photoproducts and the mechanisms of their formation are discussed.

$\alpha\alpha'$ -DIBROMODIBENZYLIDENEACETONE can exist in the *trans,trans*- (I), the *cis,trans*- (II), or the *cis,cis*-form (III). Unlike *trans,trans*- $\alpha\alpha'$ -dibromophorone,² *trans,trans*- $\alpha\alpha'$ -dibromodibenzylideneacetone (I) is structurally incapable of undergoing deconjugation, and of yielding derivatives of cyclopentane by loss of hydrogen bromide. The impact of electrons or of photons does however lead to loss of hydrogen bromide.

$\alpha\alpha'$ -Dibromodibenzylideneacetone (I) contains only four types of hydrogen atom which could be lost as hydrogen bromide: (i) H_B vicinal to a bromine atom, whose loss would lead to an acetylene (IV), (ii) H_B non-vicinal to the same bromine atom, whose loss would lead to a cyclobutenone (V), (iii) an aromatic *ortho*-hydrogen atom, vicinal to a bromine atom, whose loss could afford a benzocyclobutene derivative (VI), and (iv) an aromatic *ortho*-hydrogen atom remote from the same bromine atom, whose loss could afford a naphthalen-2-one (VII). Primary elimination products $C_{17}H_{11}BrO$, such as (IV)–(VII), could undergo cycloadditions to afford

the principal mode of decomposition by electron impact, loss of hydrogen bromide is also a significant pathway (10%) (Scheme 1).

Irradiation of $\alpha\alpha'$ -dibromodibenzylideneacetone (I) in benzene-propan-2-ol or toluene at 30 °C under nitrogen

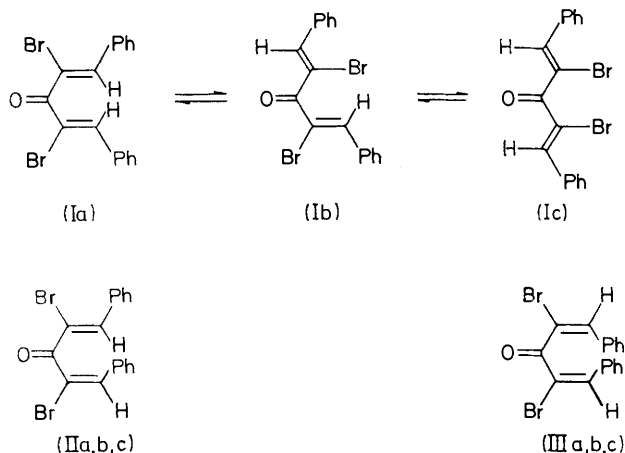


with a high-pressure mercury-vapour lamp at ca. 300 nm gave insoluble orange polymers, yellow *cis,trans*- $\alpha\alpha'$ -dibromodibenzylideneacetone (II), and four colourless compounds, isolated by column chromatography on aluminium oxide.

The ¹H n.m.r. spectrum of *cis,trans*- $\alpha\alpha'$ -dibromodibenzylideneacetone (II), in comparison with that of the *trans,trans*-isomer (I), reflected the absence of a plane of symmetry, and the different environments of the two vinylic hydrogen atoms and of the two phenyl groups. The mass spectrum indicated that, although loss of bromine is the principal mode of decomposition, loss of hydrogen bromide is also a significant pathway (8%) (Scheme 2).

Refluxing the *cis,trans*-isomer (II) with a trace of iodine in chloroform afforded the *trans,trans*-isomer (I).

A minor photoproduct from (I), $C_{17}H_{11}BrO$, showed a singlet ¹H n.m.r. signal for one vinyl proton at δ 8.38 (H_A), another singlet for one vinyl proton at 6.95 (H_B), a multiplet for two aromatic *ortho*-protons centred at 7.50, and a multiplet for seven aromatic protons centred at 7.33. The mass spectrum exhibited the appropriate pair of parent peaks M^+ 312 and 310 (1 : 1), the base peak at m/e 28, and the simple fragmentation pattern given in Scheme 3. The formation of a naphthalen-2-one (VIIa or b) is readily explicable: photochemical transformation of the *trans,trans*-isomer (I) gives the



dimers, $C_{34}H_{22}Br_2O_2$; alternatively loss of hydrogen bromide could occur after initial photo-rearrangement, e.g. the starting material (I), $C_{17}H_{12}Br_2O$, could undergo cycloaddition to yield dimers, $C_{34}H_{24}Br_2O_2$, which by double dehydrobromination could furnish dimers, $C_{34}H_{22}Br_2O_2$.

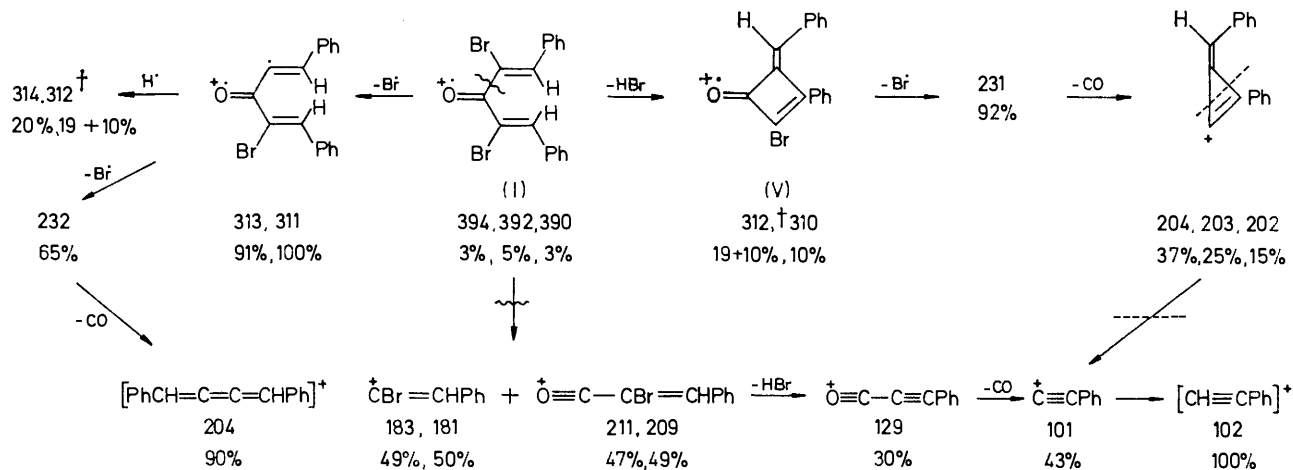
The mass spectrum of *trans,trans*- $\alpha\alpha'$ -dibromodibenzylideneacetone (I) shows that, although loss of bromine is

¹ Part VIII, C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1975, 2210.

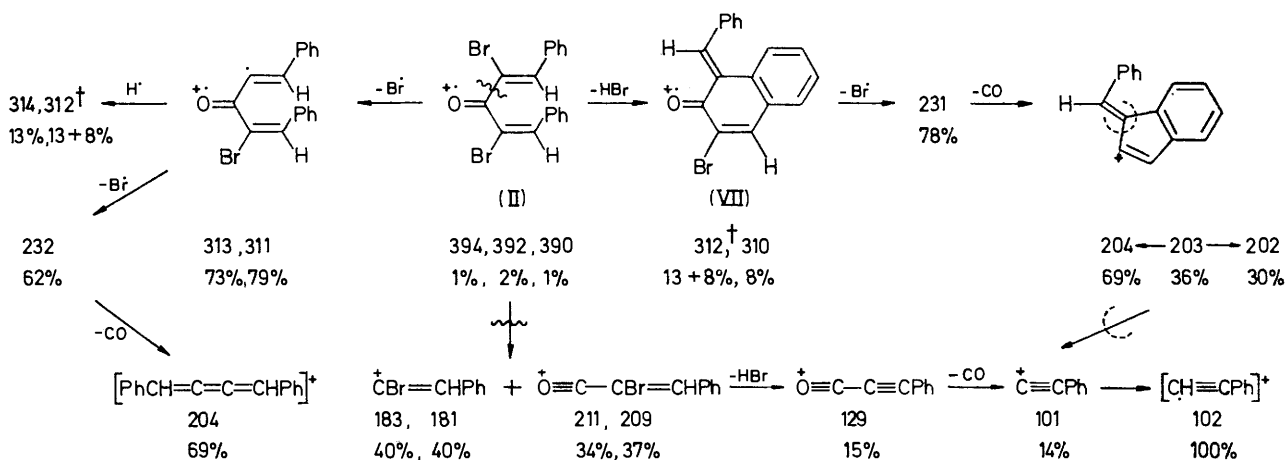
² C. W. Shoppee and Y.-S. Wang, *J.C.S. Perkin I*, 1975, 1595.

cis-trans- (II) or the *cis,cis*-isomer (III), which in the *s-cis,trans*-conformation [(IIb) or (IIIb)], by loss of an aromatic *ortho*-hydrogen atom as hydrogen bromide, can afford (VIIa or b), respectively. Structure (VIIa) is

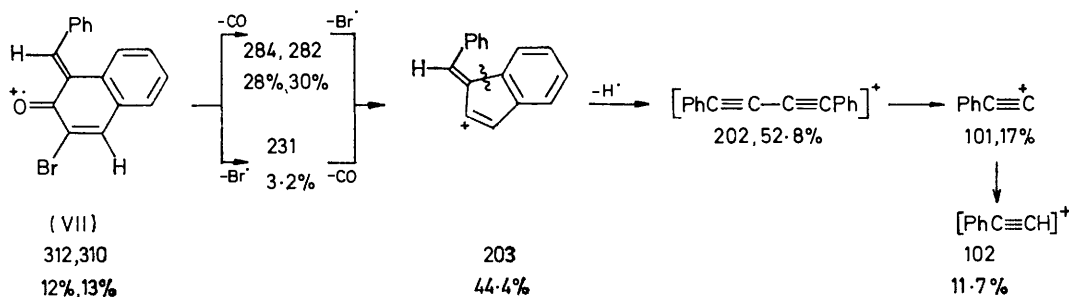
since hydrogen bonding by H_B is possible in (VIIa) but excluded in (VIIb). Hydrogen bonding is known to lead to lowering of the carbonyl stretching frequency;³ thus 1,4-dihydrophenalene,⁴ which is electronically very



SCHEME 1 $\dagger m/e$ 312 can arise (i) by way of an acyclic fragment (19%) or (ii) by the cyclisation (I) \longrightarrow (V)



SCHEME 2 $\dagger m/e$ 312 can arise (i) by way of an acyclic fragment (13%) or (ii) by the cyclisation (II) \longrightarrow (VII) (8%)



SCHEME 3

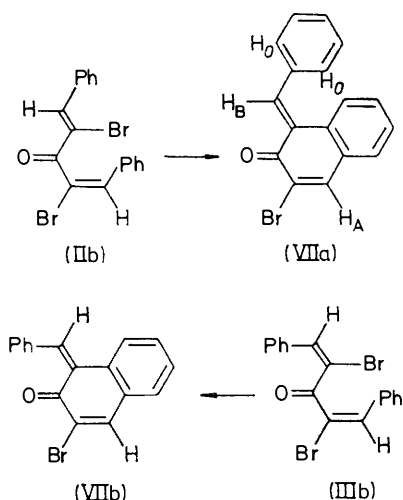
indicated by the individuality of two aromatic *ortho*-proton signals in the ¹H n.m.r. spectrum, and by the unusually low i.r. carbonyl wavenumber (1605 cm⁻¹)

³ G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960.

similar to the ketone (VIIa) and the isomeric ketone (VIIc) (see later) has ν_{max} 1637 cm⁻¹.

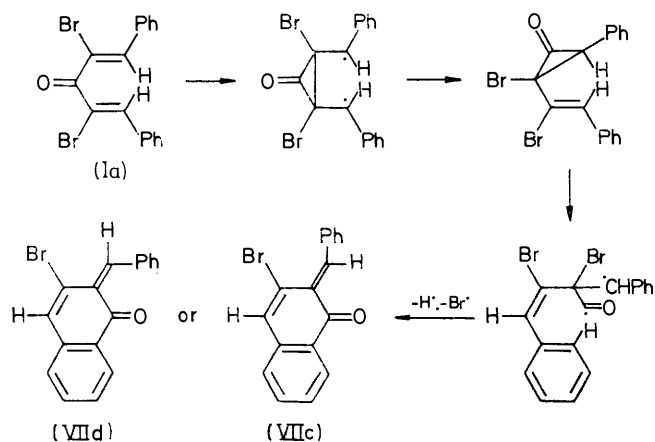
There are, however, two alternative formulae for ⁴ N. H. Cromwell and G. V. Hudson, *J. Amer. Chem. Soc.*, 1953, **75**, 872.

this photoproduct which are not excluded by the foregoing evidence. Thus a di- π -oxomethane rearrangement of the dibromo-ketone (Ia) is theoretically possible,



although no example appears to have been reported.⁵ Such a rearrangement could lead to the stereoisomeric ketones (VIIc) and (VIId), of which the latter would be excluded by the absence of hydrogen bonding to the carbonyl group.

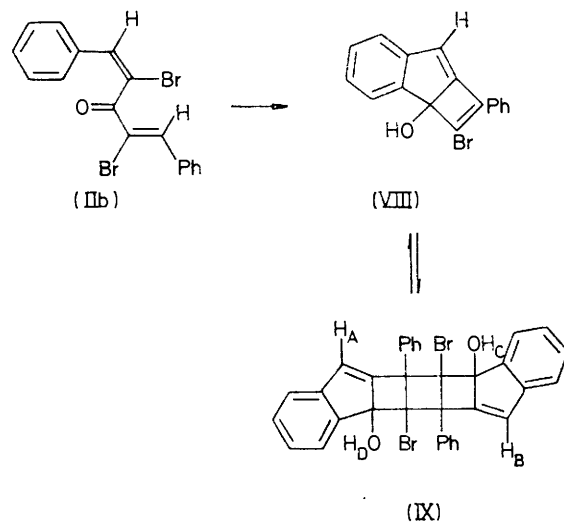
A second minor photoproduct contained a hydroxy-group but no carbonyl group (i.r.). The ^1H n.m.r. spectrum (solvent deuteriochloroform) exhibited three singlets for isolated protons at δ 6.04, 6.50br, and 8.12, a multiplet for four aromatic *ortho*-protons centred at δ 7.64, and a multiplet for fifteen aromatic protons centred at δ 7.36; use of hexadeuteriobenzene as solvent disclosed four singlet signals for isolated protons at δ 6.12, 6.36, 7.37, and 7.99, the signal at δ 7.37 being



masked in deuteriochloroform by the aromatic multiplet at δ 7.36. Deuterium exchange at 35 °C did not alter the spectra, but was not carried out in the presence of hydroxide ions. The mass spectrum showed a pair of

⁵ H. Zimmerman, University of Wisconsin, personal communication.

intense isotopic peaks at M^+ 312 and 310 (1 : 1) ($\text{C}_{17}\text{H}_{11}\text{BrO}$) and even more intense peaks at m/e 311 and 309 (1 : 1), suggesting the presence of a labile hydrogen atom; a lack of peaks prior to a trio at m/e 231, 230, and 229 ($M - ^{81}\text{Br}$, $M - ^{79}\text{Br}$, $M - \text{H}^{81}\text{Br}$, $M - \text{H}^{79}\text{Br}$, and $M - \text{HBr} - \text{H}$) confirmed the absence of a ring carbonyl group ($M - 28$); no peaks at m/e 624, 622, and 620 were observed. The ^1H n.m.r. spectral integral for twenty-two protons is consistent only with a fragile dimer $\text{C}_{34}\text{H}_{22}\text{Br}_2\text{O}_2$, which fails to show the parent isotopic mass spectral peak cluster, and breaks up symmetrically by electron impact to give the monomer $\text{C}_{17}\text{H}_{11}\text{BrO}$. We tentatively suggest the dimeric structure (IX), which can be derived from *cis,trans*- α' -dibromodibenzylideneacetone (II) in the *s-cis,trans*-conformation (IIb) by way of the monomer (VIII) formed by intramolecular reduction of the carbonyl group.⁶



The major photoproduct (*ca.* 8% yield), $\text{C}_{34}\text{H}_{22}\text{Br}_2\text{O}_2$, gave no yellow colour with tetranitromethane-chloroform. The ^1H n.m.r. spectrum showed only two doublets, centred at δ 3.38 (J 5 Hz) and 4.08 (J 5 Hz), forming an AB system (spin-decoupling of either signal caused the other to collapse to a singlet), and two signals for aromatic protons, centred at δ 7.15 (16 H) and 7.6 (4 H) (each of width 10.5 Hz), showing that there are two pairs of phenyl groups, with the four *ortho*-protons of one pair, Ph_X , in a different environment from the four *ortho*-protons of the other pair, Ph_Y . The simplicity and form of the ^1H n.m.r. spectrum, which shows the absence of a plane of symmetry in the molecule, leads us to propose the secocubane structure (X). Formula (X) is also in agreement with the observation of two carbonyl stretching frequencies ($\Delta\nu$ 85 cm^{-1}). In cubane the separation d (C-C) is 1.55 Å,⁷ so that this will be the approximate distance between the carbonyl carbon atoms, constrained by the secocubane structure, in (X); the π -orbitals of the two carbonyl groups can therefore overlap and interact,

⁶ J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, New York, 1966, 5-2C, p. 385.

⁷ E. B. Fleischer, *J. Amer. Chem. Soc.*, 1964, **86**, 3889.

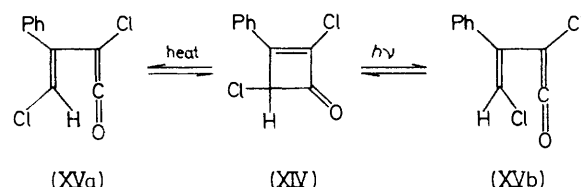
with splitting of the energy levels. Similar observations have been made for tris-homosecubane-1,7-dione,⁸ and for trifluoroacetic anhydride⁹ and other compounds¹⁰

aluminium hydride (*cf.* ref. 11) gave a colourless bromine-containing product (69%), isolated by virtue of its insolubility in ether and all common solvents except

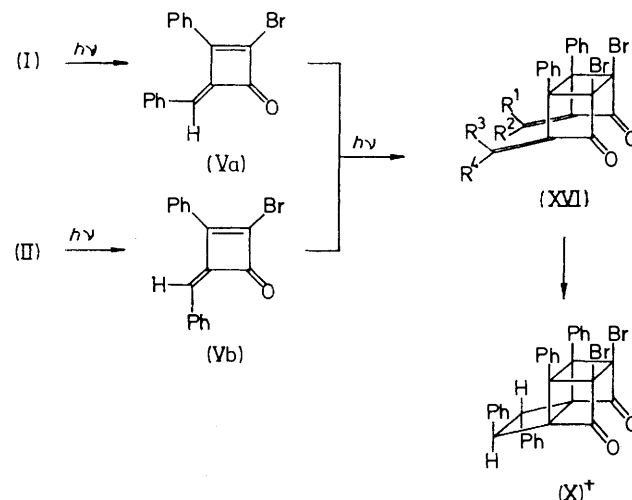
peaks. It thus appears that the diol (XI) tends to split into two halves on electron impact.

Reduction of the dibromo-diketone (X) with zinc-acetic acid furnished in poor yield a bromine-free product, $C_{34}H_{26}O_2$, M^+ 466. The 1H n.m.r. spectrum showed a broad multiplet signal for twenty aromatic protons centred at δ 7.11, and signals for six protons forming an AMX pattern of three quartets centred at δ 4.61, 3.13, and 2.40 (J_{AM} 7, J_{AX} 2, J_{MX} 19 Hz) and an A'M'X' pattern of three apparent quartets centred at δ 4.35, 2.95, and 2.53 ($J_{A'M'}$ ca. 7.5, $J_{A'X'}$ ca. 2, $J_{M'X'}$ 18 Hz). For the AMX system, irradiation at δ 4.6 caused the quartet at δ 3.1 to collapse to a doublet; irradiation at δ 3.0 altered the signal centred at δ 2.4, and caused the signal centred at δ 4.6 to collapse to a singlet; irradiation at δ 2.4 caused the quartet centred at δ 4.6 to collapse to a doublet. Similarly, for the A'M'X' system, irradiation at δ 4.35 caused the quartet centred at δ 2.9 to become an approximate doublet; irradiation at δ 3.0 modified the signal at δ 2.9, and caused the signal centred at δ 4.35 to collapse to a singlet. These observations imply the presence of a compound with AMX and A'M'X' systems ($PhCH_A-CH_MH_X-C=O$ or $PhCH_XH_M-CH_A-C=O$) of equal intensity, or a ca. 1 : 1 mixture of two isomeric compounds, each of such symmetry that it contains two identical AMX systems and thus affords an AMX spectrum even though it has six non-aromatic protons. Exchange with deuterium oxide did not alter the spectrum [absence of hydroxy-group(s)] but in the presence of sodium hydroxide unexpectedly caused the quartet at δ 4.6 (H_A) to become a doublet, with partial change of the M (+ M') and X (+ X') parts of the spectrum. The only structures that we can devise to account for the foregoing facts are the *cis*- and *trans*-forms of formulae (XII) and (XIII). These are consistent with the observed mass spectral fragmentation pattern containing peaks at m/e 438 ($M - CO$) [but not 410 ($M - 2CO$)], 389 ($M - Ph$), 376 ($M - Ph\dot{C}H$), 375 ($M - PhCH_2$), 362 ($M - Ph\dot{C}HCH_2$ or $M - PhCH_2\dot{C}H$), 335 ($M - PhCH=CHCO$), and 334 ($M - Ph\dot{C}HCH_2CO$ or $M - PhCH_2\dot{C}HCO$); the observed i.r. carbonyl frequency, ν_{max} 1700 cm^{-1} , does not however agree with that, ν_{max} 1770 cm^{-1} , reported¹² for 3-phenylcyclobut-2-enone, or with the value, ν_{max} ca. 1724 cm^{-1} , stated¹³ to be characteristic of cyclobutenones. We had anticipated either (i) *vic*-elimination of the *cis*-3,4-bromine atoms in (X) and reduction of the resulting double bond, or (ii) direct replacement by hydrogen of the bromine atoms of the α -bromo-ketone systems in (X) to yield in either event a compound $C_{34}H_{24}O_2$. Further reduction to $C_{34}H_{26}O_2$ occurred; this could involve the weak 1,6- and 7,8-bonds of the bicyclo[2.2.0]hexane systems present in (X), since the long central bond¹⁴ in a bicyclo[2.2.0]hexane is readily reduced, *e.g.* by hydrogenation with palladium-charcoal

in methanol,¹⁵ and lead to structures of the types (XII) and (XIII). A thermal $[\pi 2_s + \pi 2_a]$ cycloreversion¹⁶ could afford two benzylidene residues, reducible to two benzyl groups [*cf.* (XIII)], with cleavage of the 1,6- and 9,10-bonds in (X).



Although synthetic chloro-phenylcyclobutenones [*e.g.* (XIV)] by thermal or photochemical rearrangement can give ketens (XVa or b),¹⁷ we suggest that the secocubanedione (X) is derived from the bromo-phenylcyclobutenones (V) arising by elimination of hydrogen bromide from the $\alpha\alpha'$ -dibromodibenzylideneacetone (I) or (II). Molecules of (Va and b) undergo a photochemical symmetry-allowed $[\pi 2_s + \pi 2_s]$ cycloaddition to yield the intermediates (XVIa; $R^1 = R^4 = H$, $R^2 = R^3 = Ph$) and (XVIb; $R^1 = R^4 = Ph$, $R^2 = R^3 = H$), which by further absorption of photons undergo subsequent symmetry-allowed $[\pi 2_s + \pi 2_s]$ cycloaddition of the two staggered benzylidene side-chains to furnish the secocubanedione (X), which as required by the 1H n.m.r. spectrum has no plane of symmetry.



† The enantiomer is produced by the alternative mode in (XVIb).

The other major photoproduct (ca. 2% yield), ν_{max} 1720 cm^{-1} , $C_{34}H_{22}Br_2O_2$, is isomeric with the secocubanedione (X). The 1H n.m.r. spectrum shows that the molecule has no plane of symmetry, and exhibits two sharp one-proton singlets at δ 2.64 and 4.18 unchanged by decoupling or expansion, and three multiplets centred at δ 6.56

¹⁵ K. Hirao, T. Iwakuma, M. Taniguchi, E. Abe, O. Yonemitsu, T. Date, and K. Kotera, *J.C.S. Chem. Comm.*, 1974, 691.

¹⁶ R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 70.

¹⁷ J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, 1967, **89**, 1537; *cf.* E. F. Jenny and J. D. Roberts, *ibid.*, 1956, **78**, 2005.

¹² S. L. Manatt, M. Vogel, D. Knutson, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 2650.

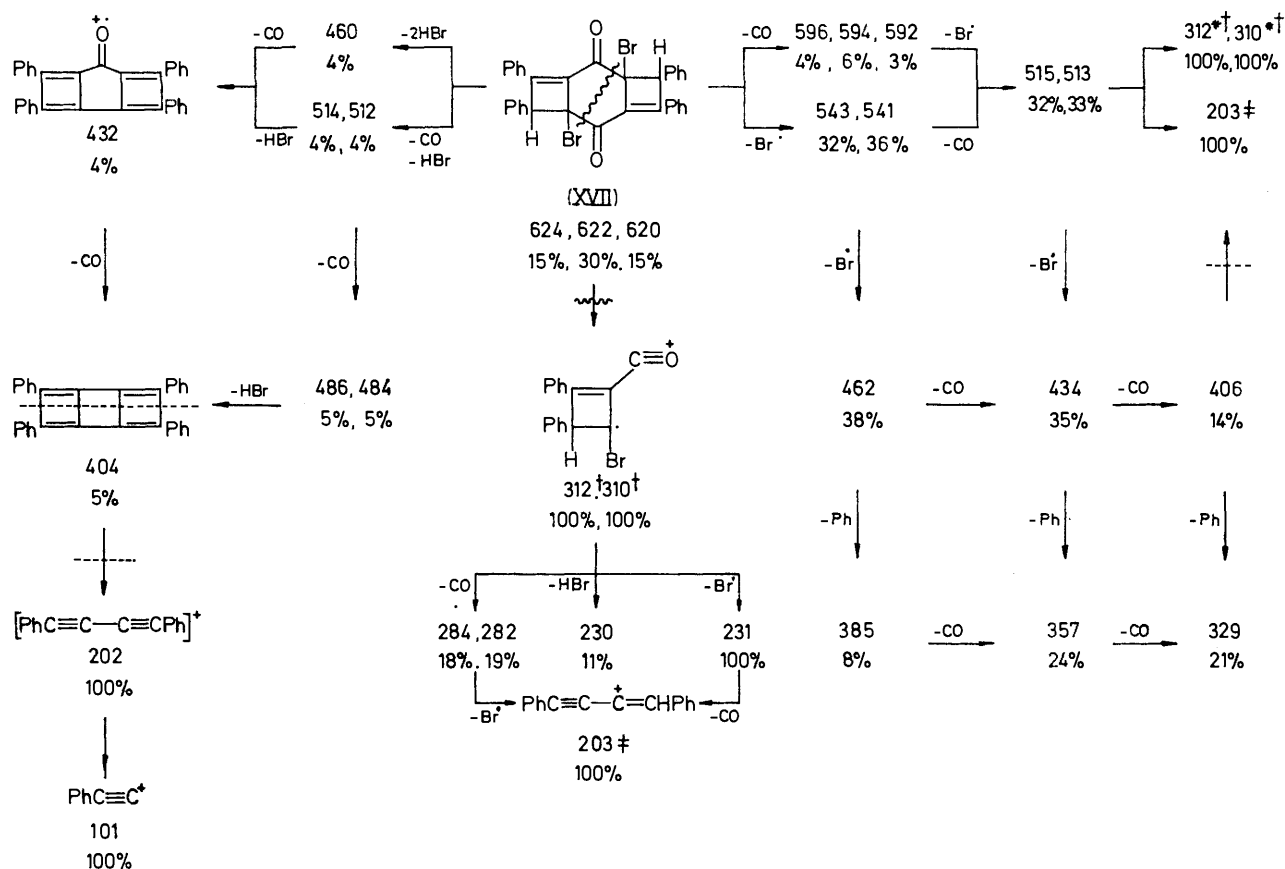
¹³ E. F. Silversmith, Y. Kitahara, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 4088.

¹⁴ B. Andersen and R. Srinivasan, *Acta Chem. Scand.*, 1972, **26**, 3468.

(2 H, width 10 Hz), 6.92 (2 H, width 10 Hz), and 7.30 (16 H). If these three multiplets are due to aromatic protons, then it seems that the molecule contains three different types of phenyl group. Since only a single i.r. maximum is observed for two carbonyl groups, these must possess similar environments. The mass spectral fragmentation pattern shows that both carbonyl groups must be in a ring, and exhibits alternate and duplicate loss of carbon monoxide, bromine, and hydrogen bromide, to give the self-consistent fragmentation pattern set out on the basis of formula (XVII) in Scheme 5.

The energy barrier between (XVIIIa) and (XVIIIb) must be greater than 10–11 kcal mol⁻¹ because both carbonyl groups must pass simultaneously through a planar configuration; a possibly considerable contribution will be derived from entropy of activation, so that the energy barrier may involve *ca.* 20 kcal mol⁻¹. The conversion of (XIXa) into (XIXb) requires passage of the same energy barrier, together with repulsive contributions arising from crowding in the resulting U-shaped molecule (XIXb), and is probably prohibited.

In the *anti*-conformers (XVIIIa and b) there are three



SCHEME 5 †*m/e* 312, 310 can arise in two ways: (i) by loss of CO and Br or (ii) by symmetrical fission of (XVII). ‡*m/e* 203 can be formed in three ways: (i) by fragmentation of *m/e* 515, 513, (ii) by symmetrical fission of *m/e* 406, or (iii) by loss of CO and Br from the cyclobutene fragment *m/e* 312, 310

The structure (XVII) must have the central six-membered ring in the boat conformation¹⁸ and can exist in an *anti*-form (XVIII) capable of assuming two conformations (XVIIIa and b), and in a *syn*-form (XIX) theoretically capable of assuming two conformations (XIXa and b). The height of the potential energy barrier between the chair and boat conformations for cyclohexane was calculated¹⁹ to be 9–10 kcal mol⁻¹ and has been determined by the ¹H n.m.r. method to be 10–11 kcal mol⁻¹;²⁰ these values assume the entropy of activation to be zero.

types of phenyl group: Ph_X, Ph_Y, and 2Ph_Z. In the conformer (XVIIIa) the hydrogen atom H_A is nearly vertically above the carbonyl group CO* but is approximately coplanar with the carbon-oxygen dipole of the carbonyl group CO†; H_A thus lies in the positive conical region²¹ above the plane of the carbonyl group CO*, and will be shielded, giving a ¹H n.m.r. signal at higher field; the hydrogen atom H_B is remote from the carbonyl

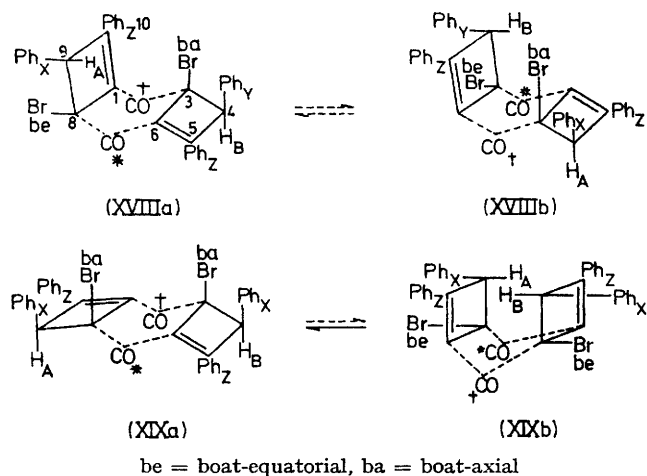
¹⁸ B. S. Green and G. M. J. Schmidt, *Tetrahedron Letters*, 1970, 4249; cf. J. Corse, B. J. Finkle, and R. E. Lundin, *ibid.*, 1961, 1.

¹⁹ C. W. Shoppee, *J. Chem. Soc.*, 1946, 1138.

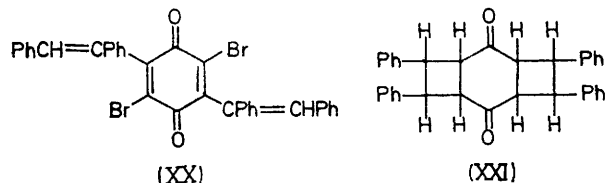
²⁰ R. K. Harris and N. Sheppard, *Proc. Chem. Soc.*, 1961, 418; F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, 1962, 84, 386.

²¹ N. S. Bhacca and D. H. Williams, 'Applications of NMR Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, 28.

group CO*, lies near to and approximately in the horizontal plane of the carbon-oxygen dipole of the carbonyl



group CO†, and will therefore be deshielded giving a ^1H n.m.r. signal at lower field. In the conformer

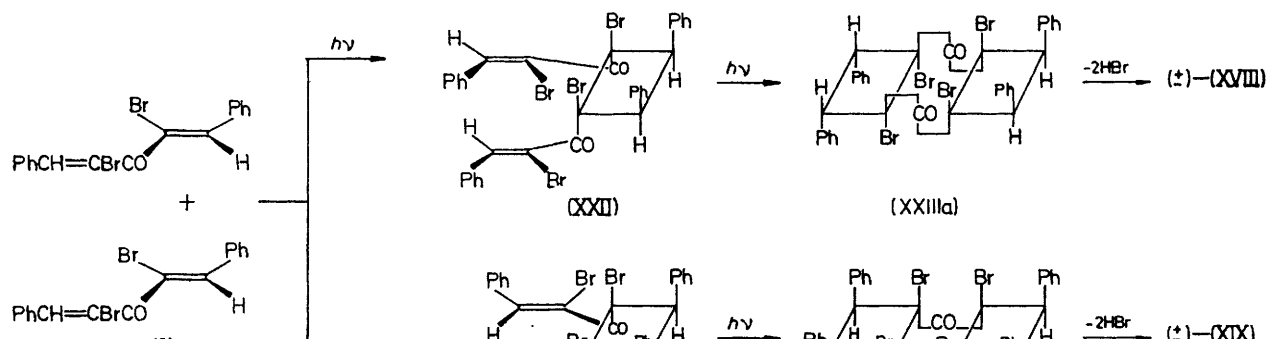


(XVIIIb), the situations of H_B (with respect to the carbonyl group CO*) and of H_A (with respect to the

for one proton, at δ 2.64 and 4.18 were unchanged, thereby confirming that there is no interconversion of the conformers (XVIIIa) and (XVIIIb) up to 110 °C in deuteriochloroform. In the *syn*-conformer (XIXa) [and the congested U-shaped *syn*-conformer (XIXb)] there are only two types of phenyl group, 2Ph_x and 2Ph_z ; atoms H_A and H_B clearly have the same environments, and should give one singlet signal for two protons. We therefore suggest the structure (XVIIIa) or (XVIIIb).

Thermal treatment of the diketone (XVIII) led to brown decomposition products without production of colour such as might have accompanied rearrangement to the quinone (XX). Hydrogenation of (XVIII) with palladium-charcoal in ethanol gave a mixture containing some unreduced starting material, λ_{max} 305 nm, ν_{max} 1720 cm^{-1} , and bromine-free stereoisomeric reduction products (XXI), λ_{max} 280 nm, ν_{max} 1700 cm^{-1} , which we were unable to separate, but whose general structure is confirmed by the mass spectrum. This disclosed the presence of traces of (XVIII) (M^+ 624, 622, and 620; 1 : 2 : 1), with the major peaks at M^+ 468 (65%) and 467 (100%), corresponding to (XXI); this identification is confirmed by a peak at m/e 234 (65%) corresponding to dibenzylideneacetone, and arising by symmetrical fission of its dimer* (XXI), and at m/e 131 and 102 for its expected fragmentation products ($\text{PhCH}=\text{CHCO}^+$ and $^+\text{CH}=\text{CHPh}$).

The formation of the tricyclic structures (XVIII) and (XIX) can be rationalised as follows. Two head-to-head eclipsed molecules of (I) can undergo a photochemical symmetry-allowed $[\pi 2_s + \pi 2_s]$ cycloaddition to give



addition of the two eclipsed α -bromobenzylidene residues to (XXIIIa or b), which by symmetrical photochemical *trans*-elimination of two molecules of hydrogen bromide furnish the *anti*-(\pm)-pair represented by (XVIII) or the *syn*-(\pm)-pair represented by (XIX).

An analogous analysis can be made for the [$\pi 2_s + \pi 2_s$] cycloaddition of the two α -bromobenzylidene residues in (XXII) if staggered, but leads to an equimolecular mixture of (\pm)-(XVIII) and (\pm)-(XIX). Molecular models suggest that [$\pi 2_a + \pi 2_a$] cycloaddition of two orthogonal α -bromobenzylidene residues in (XXII) is possible, but this appears to lead to stereochemically improbable structures.

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 solutions) were measured with Beckman Acta III and Carey 118C spectrometers; i.r. spectra (solutions in chloroform * unless otherwise specified) were determined with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were recorded with a Varian XL100 instrument for solutions in deuteriochloroform unless otherwise specified with tetramethylsilane as internal reference. Mass spectra were measured with a Varian MAT 311 double-focus spectrometer coupled to a Varian SS102 16K computer. 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.

trans-trans-2,4-Dibromo-1,5-diphenylbenta-1,4-dien-3-one

3 070, 1 615, 1 585 (all w), 1 450, 1 395, and 1 240 (all s) cm^{-1} ; for ^1H n.m.r. and mass spectra see text [Found (after drying at 40–60° and 0.01 mmHg): C, 65.7; H, 3.7%; M^+ , 311.9941, 310. $\text{C}_{17}\text{H}_{11}\text{BrO}$ requires C, 65.6; H, 3.55%; M , 311.9974, 310]. Elution with ether–benzene (1 : 19, 2 l) gave a brown gum (220 mg), ν_{max} 1 710, from which no crystalline material was obtained. Elution with ether–benzene (1 : 9; 0.5 l) gave a brown oil (30 mg), which deposited colourless prisms; trituration with acetone gave the impure secocubanedione (X) (5 mg), m.p. 188–199° (decomp.), mixed m.p. 192–202° (decomp.), ν_{max} 1 775 and 1 710 cm^{-1} . Further elution with ether–benzene (1 : 9; 3 \times 600 ml and 1 : 4; 600 ml) gave brown oils which deposited crystals. These fractions were combined (320 mg) and triturated with ether to give colourless prisms (60 mg), which by recrystallisation from ethyl acetate yielded 1-benzylidene-3-bromonaphthalen-2(1H)-one (VIIa), m.p. 162°, λ_{max} 240, 281, and 327 nm (log ϵ 3.6, 3.9, and 3.1), ν_{max} 1 605 cm^{-1} , δ 6.95 (s, H_B), 7.35 (m, 7 ArH), 7.57 (m, 2 *o*-ArH), and 8.38 (s, H_A); for mass spectrum see Scheme 3 [Found (after drying at 20° and 0.01 mmHg): C, 65.45; H, 3.55%; M^+ , 312.001, 310.0024. $\text{C}_{17}\text{H}_{11}\text{BrO}$ requires C, 65.6; H, 3.55%; M , 311.9974, 309.9993]. The ether-soluble material was recovered and triturated with acetone to give the dibromo-diketone (XVII) [\equiv (XVIII)] (10 mg), m.p. 219–224° (decomp.), as pale yellow prisms (from chloroform–ethyl acetate), λ_{max} 305 nm, ν_{max} 1 720 cm^{-1} . The ether-soluble material after separation of (VIIa) and the acetone-soluble material after separation of (XVII) [\equiv (XVIII)] was combined (260 mg) and rechromatographed on a column (1.2 \times 29 cm) of neutral aluminium oxide (20 g) in benzene; elution with ether–benzene (1 : 9, 3 \times 75 ml) gave three fractions: (i) mainly (XVIII) (24 mg); (ii) a mixture of (VIIa) and (XVIII) (16 mg); (iii) mainly (VIIa) (140 mg), which by stirring with ether gave colourless prisms (90 mg), m.p. 160–162° mixed m.p. 162°. Further

form-ethyl acetate; λ_{max} 222 and 286 nm ($\log \epsilon$ 4.32 and 4.22), ν_{max} 1 790, 1 705, and 1 690 cm^{-1} , for ^1H n.m.r. and magnetic c.d. spectra see text; for mass spectrum (m/e > 200) see Scheme 4; m/e 175 (24%), 152 (23), 151 (25), 149 (23), 129 (100, $\text{PhC}\equiv\text{C}\cdot\text{CO}^+$), 116 (43), 105 (100, C_8H_9^+), 101 (100, $\text{PhC}\equiv\text{C}^+$), 91 (24, PhCH_2^+), and 77 (69, Ph^+) [Found (after drying at 20° and 0.01 mmHg): C, 64.75; H, 3.5; Br, 25.95 (Tempe, Arizona); C, 64.75; H, 3.45% (Berlin); M^+ , 624.015, 622, and 620. $\text{C}_{34}\text{H}_{22}\text{Br}_2\text{O}_2$ requires C, 65.6; H, 3.55; Br, 25.7%; M , 623.995, 622, 620]. The low values for % carbon are probably due to tenacious retention of water, since high vacuum sublimation was excluded by thermal decomposition [Found (after drying at 120° and 0.01 mmHg over P_2O_5 for 4 h): C, 64.3; H, 3.65%]; Cookson *et al.*⁸ record that tris-homosecucubane-1,7-diones on exposure to air form monohydrates and that temperatures of 80 to >150 °C were needed before they lost water. Further elution with ether-benzene (1:49; 2 l) gave an orange oil, which by trituration with ethyl acetate yielded pale yellow crystals (120 mg); recrystallisation from chloroform-ethyl acetate then gave 1,6-dibromo-4,5,9,10-tetrahydrotricyclo-

form-benzene (50 and 70% CHCl_3 ; 1.75 l and 1.5 l) and finally with chloroform (7.5 l) gave a viscous reddish-brown oil (2.72 g), which deposited colourless prisms; trituration with ethyl acetate gave compound (X) (273 mg), m.p. 199–201° (decomp.), ν_{max} 1 790, 1 705, and 1 690 cm^{-1} .

Isomerisation of the cis,trans- (II) to the trans,trans-Isomer (I).—The isomer (II) (18 mg), m.p. 76–77°, dissolved in chloroform (4 ml), was refluxed with a trace of iodine for 24 h. Evaporation at 10 mmHg gave a dark brown residue; this was dissolved in the minimum amount of ethanol and inoculated with (I) to give the isomer (I), m.p. and mixed m.p. 95–98°. Isomerisation did not occur with iodine in refluxing carbon tetrachloride; crystallisation of the product from ether-pentane gave crude (II), m.p. 62–74°, and a further quantity, m.p. 60–74°, was obtained from the mother liquor.

Reduction of the Dibromosecucubanedione (X).—(a) *With lithium aluminium hydride.* The diketone (X) (100 mg) suspended in tetrahydrofuran (50 ml) was refluxed with an excess of lithium aluminium hydride for 4 h. The product, isolated in the usual way, was partly insoluble in ether (60 mg); this colourless solid was insoluble in all common

204, 203, 202 (6, 7, 9, $[\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}]^+$ 12%), 193, 192, 191 (6, 8, 17%), 181 (11%), 179, 178 (5, $[\text{PhC}\equiv\text{CPh}]^+$ 10%), 142, 141 (8, 6%), 131 ($\text{PhCH}=\text{CHCO}^+$ 9%), 115 (14%), 105, 104, 103 ($\text{PhCH}_2\text{CH}_2^+$ 19, 6, 9%), 91 (PhCH_2^+ 21%), and 28 (CO, 16%) [Found (after drying at 40–60° and 0.01 mmHg): C, 87.4; H, 5.55; M^+ , 466.1925. Calc. for $\text{C}_{34}\text{H}_{26}\text{O}_2$: C, 87.5; H, 5.6%; M , 466.1932].

Hydrogenation of the Dibromo-diketone (XVIII).—The dibromo-diketone (70 mg) in ethanol (10 ml) was shaken in hydrogen with 10% palladium-charcoal overnight (uptake ca. 6 ml). The product was partly insoluble in ether and yielded a brown polymer, insoluble in chloroform; the ethereal solution gave an oil (50 mg), which by treatment with ether-pentane furnished a yellowish solid, m.p. 96–101°, ν_{max} 1720 and 1700 cm^{-1} , giving a positive Beilstein test. This solid, by dissolution in ethyl acetate and addition of ether followed by filtration, gave a little starting material, λ_{max} 305 nm, ν_{max} 1725 cm^{-1} ; evaporation of the filtrate gave a yellow semisolid, λ_{max} 280, ν_{max} 1720sh and 1700 cm^{-1} . T.l.c. on silica in ether-benzene (3 : 7) gave one large

yellow spot, which by extraction with methylene chloride yielded a mixture of starting material (XVIII) and reduction products (XXI) as indicated by the i.r. (ν_{max} 1720 and 1700 cm^{-1}) and mass spectra [small peaks for (XVIII) at M^+ 624, 622, 620 (1 : 2 : 1), and major peaks for (XXI) at M^+ 468 (100%) and m/e 467 (100%)] ; other peaks were observed at m/e 450 ($M - \text{H}_2\text{O}$), 440 ($M - \text{CO}$), 430, 391 ($M - \text{Ph}$), 234 ($[\text{PhCH}=\text{CHCOCH}=\text{CHPh}]^+$), 220, 215, 206 ($[\text{Ph}_2\text{C}_4\text{H}_4]^+$), 190, 131 ($\text{PhCH}=\text{CH}^+$), 115, 105, 103 ($\text{PhCH}=\text{CH}^+$), and 28 (CO).

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