Electrocyclic Reactions. Part VII.[1] Irradiation of 3,5-Dibromo-2,6-dimethylhepta-2,5-dien-4-one (αα'-Dibromophorone)

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Irradiation of 3,5-dibromo-2,6-dimethylhepta-2,5-dien-4-one in hexane under nitrogen at *ca.* 300 nm yields, as the major product, 2-bromo-5-isopropylidene-3-methylcyclopent-2-enone. The minor product is a symmetrical photodimer, $(C_9H_{10}O)_2$, of tricyclo[5.3.0.0^{2,6}]decane type, produced by a $[_\pi2_s + _\pi2_s]$ process; it is susceptible to autoxidation in air.

IRRADIATION of 2,6-dimethylhepta-2,5-dien-4-one (phorone) [2,3] (I) in hexane or methanol gives mainly the singly deconjugated isomer [4] (II), with a little of the doubly deconjugated isomer [4] (III) and polymeric material. No carbocyclic products were detected when aqueous methanol was used,[2] although the dihydropyran (V) was isolated when

dry methanol was employed.[3] The photoconversions (I) ⟶ (II) and (II) ⟶ (III) involve hydrogen abstraction from the γ-position by the carbonyl oxygen atom,[5] a process that is facilitated by the preferred *s-cis,s-cis*-conformation (Ia) of phorone.[6-8] The mechanism suggested [3] for formation of the photoproduct (V)

[1] Part VI, C. W. Shoppee and G. N. Henderson, *J.C.S. Perkin I*, 1975, 765.

[2] K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc. (C)*, 1966, 571.

[3] P. J. Cropp and T. W. Gibson, *J. Chem. Soc. (C)*, 1967, 143.

[4] E. C. Craven and W. R. Ward, *J. Appl. Chem.*, 1960, **10**, 18.

[5] N. C. Yang and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1963, **85**, 1698; *Tetrahedron Letters*, 1964, 1203.

[6] R. B. Woodward, *J. Amer. Chem. Soc.*, 1940, **62**, 1208.

[7] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

[8] H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc. (B)*, 1966, 75.

appears to involve the *s-trans,s-trans*-conformation (Ib) of phorone, which, as the hemiacetal, is converted by
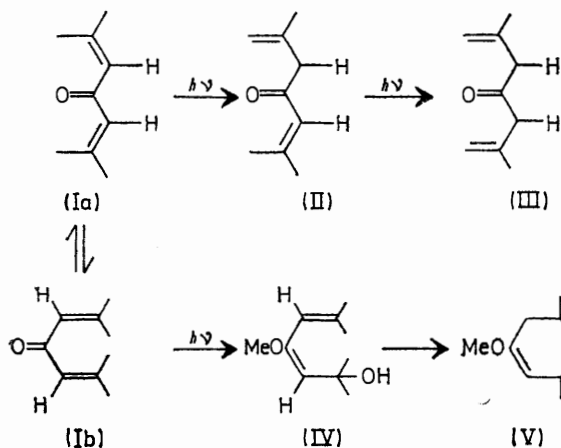
anionotropy into the intermediate (IV), cyclised by prototropy to the dihydropyran (V).

3,5-Dibromo-2,6-dimethylhepta-2,5-dien-4-one can exist in three conformations (VIa—c). A detailed investigation [8] of the u.v., i.r., and n.m.r. spectra of phorone and the dibromo-derivative (VI) suggests that the preferred conformation of the latter is a nonplanar version of the *s-cis,s-cis*-form (VIa). However, since a thermal ground state electrocyclic reaction is the predominant, if not exclusive, pathway when the dibromo-derivative is treated with acids,[9] and must
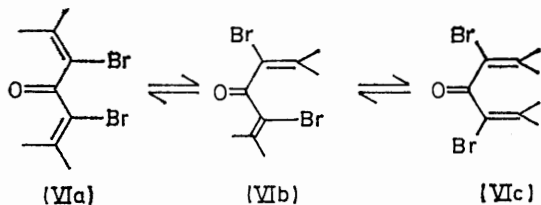
involve the *s-trans,s-trans*-conformation (VIc), we have explored the photochemical excited state reactions of the dibromo-compound in the hope of isolating carbocyclic products.

Irradiation of the dibromide (VI) in hexane through quartz at 30 °C for 16 days at *ca.* 300 nm (Corex filter) in nitrogen gave an insoluble brown polymer, which was removed each day, and a complex mixture of products. Column chromatography on neutral alumina gave some starting material, possibly accompanied by the deconjugated isomer(s) [*cf.* (II) and (III)] which polymerised rapidly, and two colourless crystalline carbocyclic compounds.

* Irradiation at δ 3.13 (H_C) gives a nuclear Overhauser enhancement of the Me_D signal (12.5%) but not of the Me_B signal, because Me_B has an alternative means of relaxation.

[9] C. W. Shoppee and R. E. Lack, *J. Chem. Soc.* (*C*), 1969, 1346.
[10] G. Hüppi, G. Eggart, S. Iwasake, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1966, **49**, 1986; S. Iwasaki and K. Schaffner, *ibid.*, 1968, **51**, 557; A. Tuinman, S. Iwasaki, K. Schaffner, and O. Jeger, *ibid.*, 1968, **51**, 1778; O. Jeger and K. Schaffner, *Pure Appl. Chem.*, 1970, **21**, 247.

The major photoproduct is 2-bromo-5-isopropylidene-3-methylcyclopent-2-enone (IX), and arises from the *s-cis,s-trans*-dibromide (VIb), possibly by hydrogen abstraction from one γ-carbon atom to yield the photoenol (VII), which is cyclised by a photochemical (or a dark) reaction involving loss of a bromine atom to give the intermediate (VIII), transformed into (IX). A possible alternative mechanism involves the known photochemical reaction of α-halogeno-ketones to give cationic or equivalent radical species.[10]

The structure (IX) is supported by the u.v. and i.r. spectra [$\lambda_{max.}$ 265 nm (log ϵ 4.33) (calc.[11] 265 nm), $\nu_{max.}$ 1 690, 1 650, and 1 615 cm^{-1}]. The ^{1}H n.m.r. spectrum,
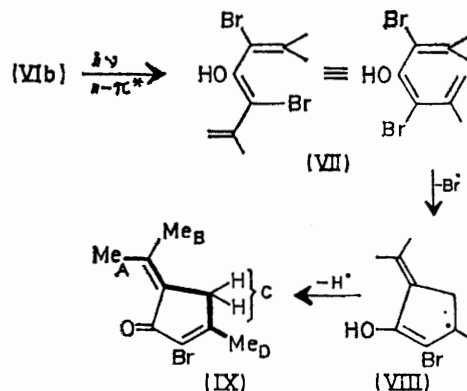
at first glance, appeared to comprise only four singlet signals δ 1.89, 2.16, and 2.33 (3 × MeC=) and 3.13 (CH$_2$), but suitable expansion disclosed long-range couplings. The signal at δ 2.33 is assigned to Me_A on chemical shift grounds; [12a] that at δ 1.89 is assigned to Me_B because the homoallylic coupling constant J_{AC} (0.95 Hz) is larger than J_{BC} (*ca.* 0.6 Hz); [13] and the
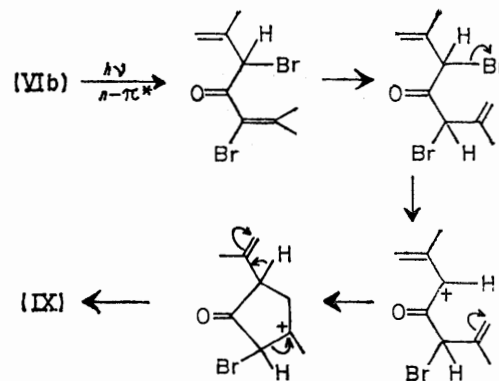
signal at δ 2.16 is assigned to Me_D.* There is a substantial 'isopropylidenic' coupling [14] between the H_C

[11] J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice–Hall, Inc., New York, 1965, 11.
[12] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, (*a*) p. 223; (*b*) p. 112.
[13] M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, 1972, **94**, 1905.
[14] W. H. de Jeu, R. Deen, and J. Schmidt, *Rec. Trav. chim.*, 1967, **86**, 33.

and the Me_D (J_{CD} 0.95 Hz), and a remarkable seven-bond coupling between the Me_A and Me_D (J_{AD} 0.3 Hz).[15] The spectrum remained unaltered on attempted exchange of H_G with deuterium. The mass spectrum showed five base peaks of equal intensity, the isotopic pair M^+ 214/216 and m/e 135, 107, and 91, which form a consistent fragmentation pattern (Scheme 1).

The physical evidence for structure (IX) is conclusive, and more informative than the chemical evidence of ozonolysis to give acetone, since this ketone can be derived not only from the isopropylidene group but also from the ring structure: (IX) $\longrightarrow$ $BrCO\cdot CO\cdot CO\cdot CH_2\cdot COMe$ $\longrightarrow$ $HO_2C\cdot CO_2H + HO_2C\cdot CH_2\cdot COMe$ $\longrightarrow$ Me_2CO. Brief treatment of the unsaturated bromo-ketone (IX) with hot methanolic sodium methoxide led to decomposition.

The minor photoproduct is a symmetrical dimer, $(C_9H_{10}O)_2$, m.p. 155—157° (decomp.), λ_{max} 215 and


SCHEME 1
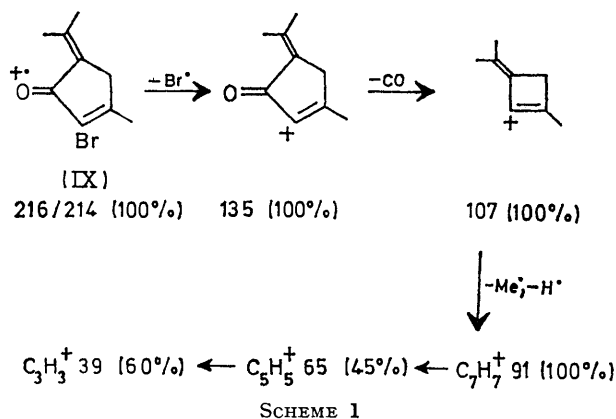
262 nm, ν_{max} 1 703 cm^{-1}, M^+ 268, formed from the dibromo-compound (VI) by overall loss of two molecules of hydrogen bromide. It is a derivative of tricyclo-[5.3.0.0^{2,6}]decane possessing one of the four structures (X)—(XIII). This cyclobutane dimer is difficult to purify because it undergoes autoxidation in air to give a compound, $(C_{18}H_{20}O_6)_n$; cyclopentenones are known to form hydroperoxides by autoxidation.[16-18] The ^1H n.m.r. spectrum is consistent with any of structures (X)—(XIII) and showed four narrow one-proton multiplets at δ 7.31, 6.18, 5.27, and 2.40 (H_A, H_B, H_C, H_D), a three-proton doublet of doublets centred at δ 1.99 (H_E), and a three-proton singlet at δ 1.18 (H_F). Irradiation at the frequency for H_A caused narrowing of the signal assigned to H_D, but, as these signals form a degenerate AA'XX' system, this narrowing does not give J_{AD} directly; however it is of the order of 0.5 Hz. Because of the degeneracy of this system ($\Delta\nu/J$ very large), it is impossible to obtain the internal coupling constant $J_{DD'}$, which could have differentiated the

structures (X)—(XIII). The mass spectrum showed a symmetrical fragmentation pattern, with alternating
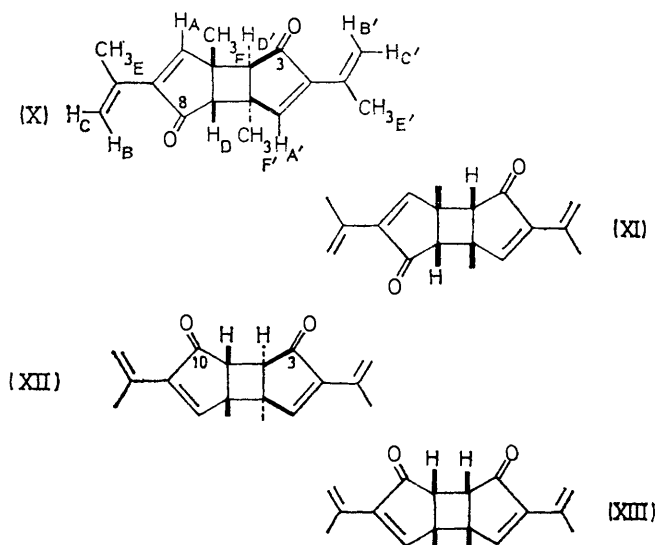
and duplicate loss of methyl groups and of carbon monoxide, consistent with the structures (X)—(XIII), which may be represented for (X) or (XI) as in Scheme 2.

SCHEME 2
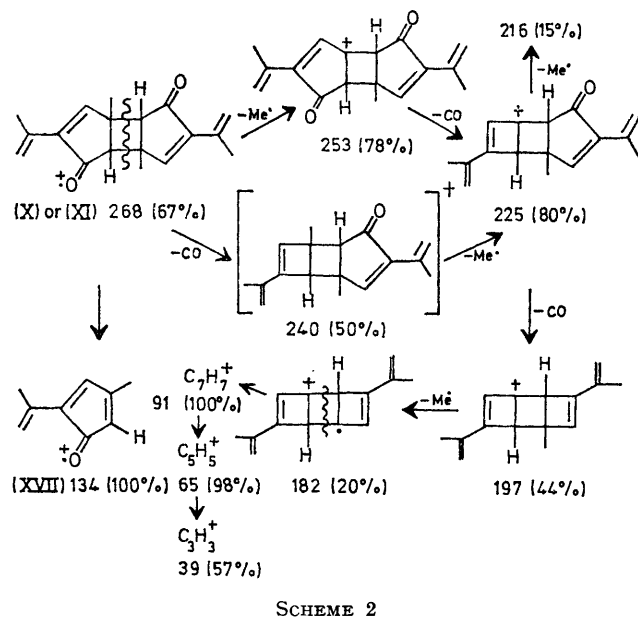
The primary photoproduct (IX), on continued irradiation, appears to undergo a series of $\alpha\beta$-$\beta\gamma$ changes to afford the sequence of isomers (XIV)—(XVI); the last

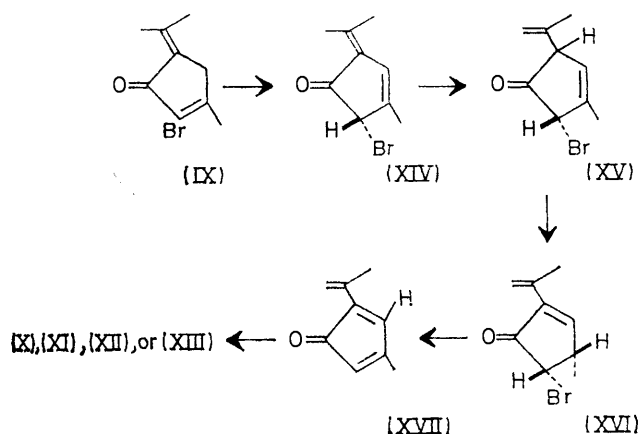[15] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.
[16] A. C. Campbell, J. McLean, and W. Lawrie, *Tetrahedron Letters*, 1969, 483.
[17] C. W. Shoppee and B. C. Newman, *J. Chem. Soc.* (C), 1969, 2767.
[18] A. Afonso, *Canad. J. Chem.*, 1969, **47**, 3693.

(XVI) by loss of hydrogen bromide furnishes the cyclopentadienone (XVII). This can dimerise by a symmetry-allowed $[_\pi 2_s + _\pi 2_s]$ head-to-tail cycloaddition of


two staggered molecules to afford the *anti*-structure (X), or of two eclipsed molecules to furnish the *syn*-structure (XI), or by a symmetry-allowed $[_\pi 2_s + _\pi 2_s]$ head-to-head cycloaddition of two staggered molecules to give the *anti*-structure (XII), or of two eclipsed molecules to yield the *syn*-structure (XIII). The analogous symmetry-allowed $[_\pi 2_a + _\pi 2_a]$ cycloadditions appear to be excluded on stereochemical grounds as leading to structures containing two cyclopentene rings *trans*-fused to a cyclobutane ring.

The apparent production of a single cyclobutane dimer contrasts with the formation from 3-methylcyclopent-2-enone by u.v. irradiation in toluene [19,20] of three cyclobutane dimers (XVIII) (*anti*, 47%; *syn*, 13%) and (XIX) (*anti* or *syn*, 21%), whose structures were assigned on the basis of the ^{1}H n.m.r. spectral data of the three compounds and their respective monolactones obtained by Baeyer–Villiger oxidation. The signal for the angular methyl groups occurs at δ 1.48 in the *syn*-dimer [as (XVIII)] but at δ 1.2 in the *anti*-dimer [as (XVIII)] and the dimer (XIX). The signal for the angular methyl groups in our unsaturated dimer appears at δ 1.18, so that the *syn*-structure (XI) can probably be eliminated; the *anti*-structure (X) or the alternative structures (XII) and (XIII) are thus most likely to be correct. The pronounced benzene-induced solvent shift for the angular methyl groups in our unsaturated dimer (0.58 p.p.m.) does not permit a distinction to be made between formula (X) and formulae (XII) and (XIII).[12b]

We attempted to determine whether our unsaturated dimer has the structure (X) by ozonolysis, further oxidation, and esterification of the acidic fraction,

since tetramethyl 1,3-dimethylcyclobutane-*r*-1,*c*-2,*t*-3,*t*-4-tetracarboxylate [21] (XX) should be formed. Ozonolysis and decomposition of the ozonide gave some formaldehyde; oxidation of the non-volatile material with chromium trioxide–acetic acid gave a small acidic fraction, which was esterified with diazomethane, but the resultant methyl ester did not crystallise when inoculated with the tetramethyl ester (XX), m.p. 75.5—77°. The main product was a wax-like neutral substance, $\nu_{max.}$ 1 715 cm^{-1}, which appeared, from its ^{1}H n.m.r. spectrum and from the fact that a mass spectrum (M^+ 430) could only be obtained when the probe was heated to 400 °C, to be a polymer $C_{16}H_{15}O_{14}$–$(C_{16}H_{14}O_{14})_n$–$C_{16}H_{15}O_{14}$ with a repeating $C_{16}H_{14}O_{14}$ unit, m/e 430, whose characteristic fragmentation pattern (see Experimental section) we are unable to interpret, but which may correspond to an oxidised polymeric hydroperoxide.

The only other reported example of the u.v. irradiation of an α-bromo-αβ-unsaturated ketone appears to be that of the compound (XXI), which undergoes a $[_\pi 2_s + _\pi 2_s]$
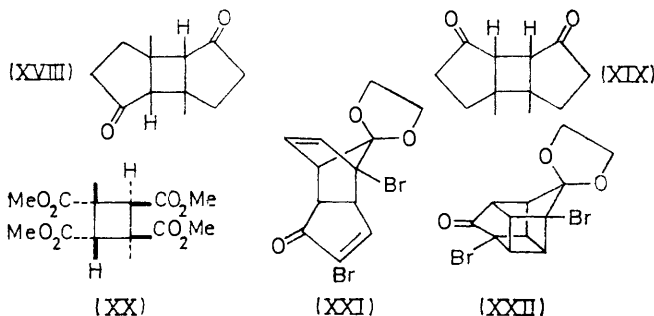
cycloaddition, with retention of both bromine atoms, to give the cubane intermediate (XXII).[22]

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 a Beckman Acta III spectrometer; i.r. spectra (solutions in chloroform * unless otherwise specified) were measured with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were recorded with Varian HA-100D, XL-100-15, and XL-100-12 instruments for 5—10% w/v 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 SS 102 16K computer. Column chromatography was performed using aluminium oxide (Woelm; neutral). High pressure liquid chromatography (h.p.l.c.) was carried out with a Waters 311 machine using an analytical Porasil

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* Solutions in chloroform give carbonyl bands *ca.* 15 cm^{-1} to lower wavenumber than solutions in carbon tetrachloride.[23]

[19] G. Mark, H. Malthäus, F. Mark, J. Leitich, D. Henneberg, G. Schomburg, I. v. Wilucki, and O. E. Polansky, *Monatsh.*, 1971, **102**, 37.
[20] R. Reinfried, D. Bellus, and K. Schaffner, *Helv. Chim. Acta*, 1971, **54**, 1517.

[21] H. Ziffer and R. J. Williams, *J. Org. Chem.*, 1968, **33**, 920; cf. W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Ber.*, 1962, **95**, 1642.
[22] P. E. Eaton and T. W. Cole, *J. Amer. Chem. Soc.*, 1964, **86**, 3157.
[23] A. R. H. Cole, *Rev. Pure Appl. Chem.*, 1954, **4**, 119.

T column (2 ft × 1/8 in) or a preparative Porasil A column (4 ft × 3/8 in) and benzene–chloroform (1 : 3) as eluant. G.l.c. was performed with a Beckman GC45 chromatograph fitted with a flame ionisation detector, using an analytical SE30 column (8 ft × 1/4 in; helium flow rate 40 ml min^{-1}; temperature 230 °C).

3,5-Dibromo-2,6-dimethylhepta-2,5-dien-4-one (VI).— Phorone tetrabromide, m.p. 87° (from ethanol) (lit.,[24] m.p. 88°), $\nu_{max.}$ (CCl$_4$) 1 735 cm^{-1} (lit.,[9] 1 740 cm^{-1}), was dehydrobrominated with pyridine at 25 °C to give the dibromide (VI), m.p. 30° (lit.,[25] 32°), $\nu_{max.}$ (CCl$_4$) 1 665 and 1 620 cm^{-1} (lit.,[9] 1 668 and 1 625 cm^{-1}) (80% yield).

Photoreaction of the Dibromide (VI).—The dibromide (100 g), dissolved in hexane, was irradiated with a Hanovia high-pressure quartz mercury-vapour lamp (No. 6 515—34) with a Corex filter (λ 260—360 nm) in a quartz apparatus in nitrogen at 30 °C for 16 days. Dark brown polymer was removed from the surface of the irradiation vessel each day, and the residual oil, obtained by evaporation of the solution after washing with sodium hydrogen carbonate and with water, was chromatographed on a column of aluminium oxide (1 500 g) prepared in hexane. Elution with benzene–hexane mixtures and with benzene gave a yellow liquid (55 g), containing the dibromide, but also the singly and doubly deconjugated isomers (it slowly darkened and polymerised); some dibromide (VI) could be isolated (m.p. 28°) by dissolution in pentane and refrigeration. Elution with ether–benzene (1 : 19, 1 : 9) gave brown oils. Further elution with ether–benzene (1 : 9) gave numerous fractions, some of which deposited colourless crystals contaminated with brown oil. These, when washed with pentane, gave 2-*bromo*-5-*isopropylidene*-3-*methylcyclopent*2-*enone* (IX), m.p. 114—118° (0.4 g), m.p. 118—119° (from ether–pentane or ethyl acetate–pentane); $\lambda_{max.}$ 265 nm (log ε 4.33); $\nu_{max.}$ 1 690, 1 650, and 1 615 cm^{-1}; for ^{1}H n.m.r. spectrum see text; m/e 216/214 (M^+), 201/199 (M − Me), 188/186 (M − CO), 173/171 (M − CO − Me), 135 (M − Br), 120 (M − Br − Me), 107 (M − Br − Me − CO), 92 (C$_7$H$_8$$^+$), 91 (C$_7H_7$$^+$), 77 (Ph$^+$), 67, 65 (C$_5H_5$$^+$), and 39 (C$_3H_3$$^+$), giving a yellow colour with tetranitromethane–chloroform [ozonolysis in chloroform at 0 °C, complete removal of chloroform at 25° and 10 mmHg, addition of water, and distillation yielded acetone (identified as iodoform, m.p. 118°, obtained by use of iodine and ammonium hydroxide in the cold)] (Found: C, 50.4; H, 5.15; Br, 37.1%; M^+ 216/214. C$_9$H$_{11}$BrO requires C, 50.25; H, 5.15; Br, 37.1%; M, 216/214). Elution with ether–benzene (1 : 4, 1 : 2, and 1 : 1) gave numerous fractions some of which deposited colourless crystals contaminated with brown oil; washing with ether furnished the di-isopropylidenedimethyltricyclo[5.3.0.0^{2,6}]decadienedione [(X), (XII), or (XIII)], m.p. 150—155° (decomp.) (0.25 g), raised by recrystallisation from methylene chloride–pentane or ethyl acetate–pentane to 155—157° (decomp.), $\lambda_{max.}$ 215 and 262 nm, $\nu_{max.}$ 1 703 cm^{-1}, giving a yellow colour with tetranitromethane–chloroform; analytical g.l.c. gave two peaks with t_R 2.8 and 11.2 min of relative areas 24 : 1, and the analysis specimen was therefore purified by h.p.l.c. (see later), sent for analysis packed in nitrogen, sealed in a high vacuum, and handled by the analyst under nitrogen (Found: C, 80.4; H, 7.5%; M^+, 268.1450. Calc. for C$_{18}$H$_{20}$O$_2$: C, 80.55; H, 7.5%; M^+, 268.1463); for mass spectrum see text; δ 1.18 (s, 3 H$_F$), 1.99 (dd, 3 H$_E$), 2.40, 5.27, 6.18, and 7.31 (all m, H$_D$, H$_C$, H$_B$, and H$_A$, respectively) (J_{BC} 2, J_{BE} 0.8, J_{CE} 1.5 Hz) [all samples showed peaks

(due to a contaminant) at δ 1.92 and 5.19, coupled by 1.6 Hz, forming part of an Me–C=CH$_2$ system]. When the n.m.r. spectrum was retaken two days later with the same solution in the same n.m.r. tube, changes were observed suggesting rearrangement or disproportionation catalysed by traces of deuterium chloride present in the solvent deuteriochloroform. Further elution with ether gave much brown oil (6.2 g), from which crystalline material could not be obtained, and finally a dark semisolid (2 g).

In a series of similar experiments for various times (8, 12, 16, and 32 days), the dibromide (100 g) gave starting and deconjugated material (85, 52, 55, and 50 g), the cyclopentenone (IX) (0.17, 0.18, 0.4, and 0.3 g), and the cyclobutane dimer [(X), (XII), or (XIII)] (0.13, 0.14, 0.23, and 0.3 g). It seems certain that these cyclic products are formed in larger quantities than the small amounts isolated. For purification of the cyclobutane dimer, a study by analytical h.p.l.c. on Porasil T in benzene–chloroform (1 : 4) (t_R 5.5 min) led to use of preparative h.p.l.c. on Porasil A in benzene–chloroform (1 : 3), which gave the dimer, m.p. 155—157° (decomp.) (t_R 21 min) but with only 48% recovery (decomposition by traces of hydrogen chloride in the solvent chloroform?). Until the sensitivity of the dimer in the solid state to atmospheric oxygen was recognised, unsatisfactory analyses were obtained, with oxygen content increasing with time prior to analysis [Found: C, 77.1, 74.8; H, 7.3, 7.0 (Tempe, Arizona); C, 69.1, 69.1; H, 6.7, 6.7 (New York): C, 64.5; H, 6.3 (Berlin). (C$_{18}$H$_{20}$O$_6$)$_n$ requires C, 65.0; H, 6.1%]; the oxidation product, m.p. >300°, appeared to be a polymeric hydroperoxide, insoluble in deuteriochloroform and hexadeuteriobenzene and giving in hexadeuterioacetone a polymer-type ^{1}H n.m.r. spectrum devoid of significant peaks.

The cyclobutane dimer (268 mg), dissolved in chloroform at 25 °C and treated with ozonised oxygen for 15 min at −70 °C, was precipitated unchanged; it was recovered, dissolved in chloroform, and treated with ozonised oxygen for 30 min at 25 °C. The solvent was removed under vacuum, water (5 ml) was added, and the flask was connected to a trap containing water (1 ml); a current of nitrogen was passed, and the ozonide–water mixture heated gradually to 100 °C. The contents of the trap contained some formaldehyde, as shown by the development of a red-brown colour on heating with a solution of resorcinol in 2N-sodium hydroxide. The contents of the flask were evaporated under vacuum; the residue was dissolved in a little acetic acid and treated with 2% chromium trioxide in acetic acid for 4 h at 25 °C; the resulting solution was worked up in the usual way and separated into acidic and neutral fractions. The acidic fraction (20 mg) was dissolved in ether and treated with ethereal diazomethane; the oily ester failed to crystallise from a trace of methanol at −10 °C when inoculated with the cyclobutane tetraester (XX).[21] The neutral fraction (85 mg) formed a wax-like semi-solid, $\lambda_{max.}$ 222, 273, and 303 nm, $\nu_{max.}$ 1 715 cm^{-1}; the ^{1}H n.m.r. spectrum in deuteriochloroform gave a polymer-type spectrum devoid of significant peaks; mass spectrometry at 400 °C (70 eV) gave peaks at m/e 430 (M^+; 7%) and 429 (18%), 415 (4%, M − Me), 371/370/369 (8, 13, 33%; M − Me − CH$_2$O$_2$), 357/356/355 (9, 11, 33%; M − Me − CH$_2$O$_2$ − CH$_2$), 341 (12%; M − Me − CH$_2$O$_2$ − 2CH$_2$); 297/296/295

[24] C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1928, 365.
[25] F. Francis and F. G. Willson, *J. Chem. Soc.*, 1913, 2238.

(8, 16, 50%; $M - Me - 2CH_2O_2 - 2CH_2$), 283/282/281 (8, 12, 44%; $M - Me - 2CH_2O_2 - 3CH_2$), 267 (8%), 223/222/221 (base peak, $M - 2$Me$ - 3CH_2O_2 - 3CH_2 + $H), 209/208/207 (9, 13, 80%), 193 (6%), 191 (9%), 149/148/147 (11, 6, 44%), 133 (9%), 115 (4%), 111 (6%), 105 (5%), 98 (6%), 97 (12%), 95 (8%), 91 (13%; $C_7H_7{}^+$), 85 (13%), 83 (16%), 81 (10%), 79 (6%), 77 (6%), 75/74/73 (7, 8, 89%, Et$_2$O?), 71/70/69/68/67 (22, 11, 19, 6, 13%), 60/59 (6, 6%); 57/56/55/54/53 (38, 15, 35, 5, 5%), 44 (16%; CO_2), 43/42/41 (40, 13, 50%; MeCO), 39 (19%; $C_3H_3{}^+$), and 28 (81%; CO).