

Thermal, Photochemical, and Acid-catalysed Rearrangements of the Spiro-dimer of α,α' -Bis(methoxycarbonyl)-*o*-quinodimethane. X-Ray Crystal Structure of *trans,trans*-Tetrakis(methoxycarbonyl)dibenzo[*a,e*]-cyclo-octene

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The spiro-dimer of α,α' -bis(methoxycarbonyl)-*o*-quinodimethane is allocated the stereochemistry (1) by comparison of its properties with those of the isomers (6a) and (6b) obtained from it by photolysis. Under acidic conditions the isomers (1) and (6a) give mainly epimeric products [the epimeric tosylates (9) with toluene-*p*-sulphonic acid, and the epimeric dibenzocycloheptenes (8a) and (8b) and lactones (11) with boron trifluoride-diethyl ether] showing that the isomers (1) and (6a) differ in configuration at the benzylic carbon adjacent to the spiro-centre. A single-crystal X-ray structure determination shows that the major thermal rearrangement product of compound (1) has structure (4) rather than the structure (2) previously proposed; the minor rearrangement product is compound (7). The thermal rearrangements of compounds (1) to (4), (6a) to (7), and (6b) to (2) are formal 1,3-shifts following the forbidden suprafacial-retention geometry; rearrangement by a radical dissociation-recombination mechanism is likely.

α,α' -BIS(METHOXYCARBONYL)-*o*-QUINODIMETHANE, generated by iodide reduction of dimethyl α,α' -dibromo-*o*-phenylenediacetate, is reported¹ to form a spiro-dimer (1) which at 140 °C rearranges by a formal 1,3-shift (1; arrows) to the dibenzo[*a,e*]cyclo-octene (2). The original assignment of stereochemistry to compound (1)¹ was restricted to the allocation of a *trans* relationship between H^B and H^C (J_{BC} 11 Hz).† It seemed likely, however, that the full stereochemistry was that shown in structure (1) which would arise through Diels–Alder dimerisation of the *E,E*-*o*-quinodimethane via the *endo* transition-state arrangement (3). Whether the conversion of compound (1) into (2) was concerted or two-step, the stereochemical course would be remarkable, involving antarafacial use of the migration framework and inversion at the migrating benzylic centre. Stemming from our interest in formal 1,3-shifts which may involve radical intermediates,^{2,3} we now report our revision of the stereochemistry of the thermolysis product of the spiro-dimer (1) [for which we propose structure (4)], as well as evidence for the stereochemistry [shown in structure (1)] of the spiro-dimer.

Involvement of the *E,E*-*o*-quinodimethane rather than its *Z,E*-isomer in dimer formation is supported by trapping with *N*-phenylmaleimide; the ¹³C n.m.r. spectrum of the adduct is fully consistent with the symmetrical structure (5), showing only twelve lines. The ¹³C n.m.r. spectrum of the related dimethyl fumarate adduct showed peaks for four distinct ester carbonyls (δ 174.39, 172.60, 171.895, and 171.35 p.p.m. from Me₄Si).

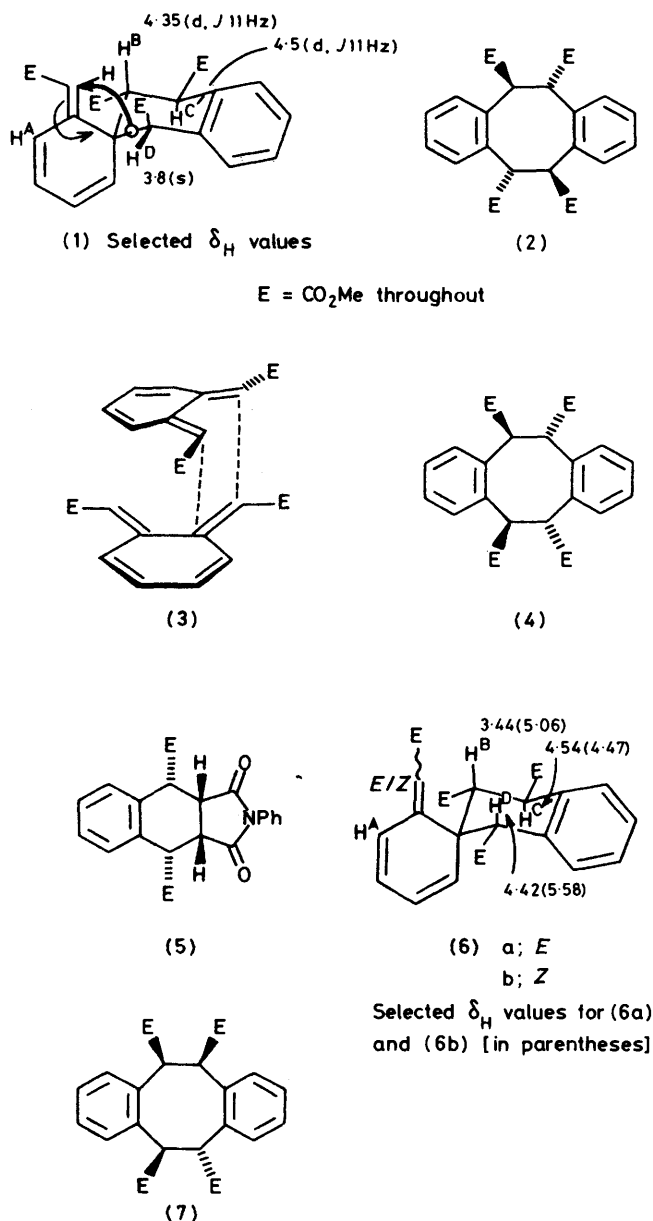
The *E*-stereochemistry about the exocyclic double bond in the dimer (1) is consistent with the failure of this compound to react with iodine in boiling benzene, and with the appearance of one olefinic proton [H^A in

(1)] at δ_H 7.75 due to strong deshielding by the *cis* ester group.

Since the dimer (1) is extensively rearranged by sodium methoxide,⁴ attempts to effect epimerisation of the axial methoxycarbonyl group were made by irradiation of compound (1) (CH₃CN solution; medium-pressure Hg lamp; 20 °C). Brief irradiation led to complete conversion of (1) into a mixture of two stereoisomers, assigned structures (6a) and (6b). More prolonged irradiation gave increasing quantities of the dibenzo[*a,e*]cyclo-octene (7); in the ¹H n.m.r. spectrum (CDCl₃ containing a little benzene) the cyclo-octene protons of (7) appeared as two AB systems (δ 4.82 and 4.97, J 9 Hz; δ 4.34 and 4.78, J 11 Hz) and this spectrum was unchanged at 115 °C.

That compounds (6a) and (6b) were *Z-E* double-bond isomers was shown by the conversion of compound (6b) into (6a) with iodine in boiling benzene; in compound (6a) the proton H^A is strongly deshielded (δ 7.68–7.93br, d, J 10 Hz) as in compound (1), whereas in isomer (6b) the olefinic protons appear together as a 5 H-multiplet (δ 5.64–6.26). The change in stereochemistry from (6a) to (6b) results in strong and roughly equal deshielding of H^D and one cyclohexene proton. Since the high-field (sharp) doublet in compound (6a) is attributed to H^B, which is deshielded in isomer (6b), then the enoate moiety, H^B, and H^D are all probably mutually *cis* in both isomers (6a) and (6b). The signals of H^C and H^D are both broadened in the spectra of isomers (6a) and (6b) but not in that of compound (1); this is consistent with benzylic and/or homobenzylic coupling involving these quasi-axial protons.⁵ The vicinal coupling constants (J_{BC}) in compounds (6a) and (6b) are 9 and 10 Hz, respectively, strongly indicating a *trans* relationship between H^B and H^C. In the adducts derived from compounds (6a) and (6b) with 4-phenyl-(4*H*)-1,2,4-triazole-3,5-dione, the corresponding coupling constants

† Numerical values for the coupling constants were not given in ref. 1.



are 12 and 13 Hz, respectively, leaving little doubt about the *trans* relationship of H^B and H^C in isomers (6a) and (6b) (see below).^{*} The structures (6a) and (6b) for the irradiation products of the dimer (1) therefore follow. Comparison of the resonance for H^B in isomers (1) and (6a) shows the expected deshielding of H^B in (1) by the axial methoxycarbonyl group.

Reaction of the isomers (1) and (6a) with toluene-*p*-sulphonic acid in boiling benzene was stereoselective; compound (1) gave a small quantity of the dibenzocycloheptene (8a), whilst the major product was one of the diastereoisomeric tosylates (9); on the other hand,

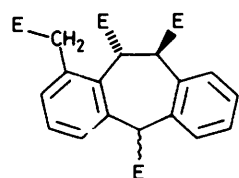
^{*} The X-ray crystal structure of compound (4) shows the *trans* disposition of each pair of vicinal cyclo-octene hydrogens and so provides good evidence for *trans* disposition of hydrogens in the cyclohexene ring of the spiro-dimer (1).

isomer (6a) gave a *ca.* 1 : 1 mixture of compound (8b) and the other epimeric tosylate (9). On hydrogenolysis both tosylates gave the same product, (10). The dibenzocycloheptenes (8a) and (8b) were major products in the reaction of compounds (1) and (6a), respectively, with boron trifluoride-diethyl ether in boiling benzene and their formation was highly stereoselective. The other major products of the boron trifluoride-catalysed rearrangement of compounds (1) and (6a) were the epimeric lactones (11). Again, compound (1) gave mainly one of these lactones and the isomer (6a) gave mainly the epimeric lactone. A further product (12), obtained from compound (1), possessed a phenyl group, no doubt derived by attack of an intermediate carbonium ion on the solvent; an analogous product was not isolated in the reaction of the isomer (6a) with boron trifluoride-diethyl ether complex in boiling benzene. Under acidic conditions compound (1) prefers intermolecular reactions but its isomer (6a) prefers intramolecular reactions; the reason for this difference is not clear at present. The formation of epimeric products from the isomers (1) and (6a) shows that these compounds differ in configuration at the benzylic carbon adjacent to the spiro-centre † and not *only* at the spiro-centre itself. However, isomers (1) and (6a) cannot differ in configuration at *both* the spiro-centre and the adjacent benzylic carbon for this would be inconsistent with strong deshielding of the non-benzylic and one benzylic cyclohexene proton in compound (6b), as well as with the thermal rearrangements discussed below. It then follows that the epimers (1) and (6a) differ only in configuration at the benzylic carbon adjacent to the spiro-centre.

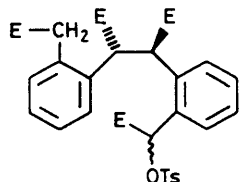
In agreement with the original work,¹ thermolysis of compound (1) in boiling xylene gave mainly one dibenzo-[*a,e*]cyclo-octene in which the protons of the cyclo-octene ring appear as a single AB-system [δ (CDCl₃) 4.68 and 5.08, *J* 8 Hz]. However, chromatography of the ethanolic mother liquor from the crystallisation of this product gave the *cis-trans*-isomer (7) in *ca.* 10% yield. Similar thermolysis of compound (6a) gave compound (7) as the only major product detected (n.m.r.), and rearrangement of the isomer (6b) gave a single, new *trans-trans*-dibenzo[*a,e*]cyclo-octene in which the cyclo-octene ring protons appear as a single AB-system [δ (CDCl₃) 4.46 and 5.19, *J* 12 Hz]. The larger vicinal coupling in this compound suggests it has structure (2), and that the rearrangement product of compound (1) should be reformulated as having structure (4). In the distorted tub (or boat) conformation⁶ dihedral angles for vicinal hydrogen on both sides of the tub can approach 180° for structure (2) but, in the isomer (4), distortion of the tub to secure a dihedral angle near 180° on one side gives a dihedral angle near 90° on the other side. Reassignment of the structure of the rearrangement product of compound (1) as (4), and assignment of

† This argument makes the reasonable assumption that the mechanisms of acid-catalysed rearrangement are the same for compounds (1) and (6a).

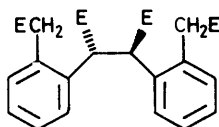
structures (7) and (2) to the rearrangement products of isomers (6a) and (6b), respectively, has the advantage that all three rearrangements then follow a suprafacial-retention geometry. This is in accord with rearrangement *via* a biradical intermediate or by the concerted-forbidden path which may be favoured by acyl substitution at the migrating centre.⁷ There is CIDNP



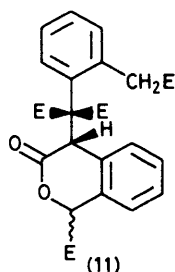
(8) a; β -E
b; α -E



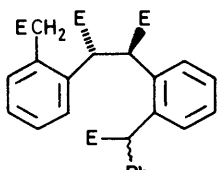
(9)



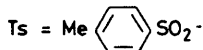
(10)



(11)



(12)



evidence that a related rearrangement follows the homolysis-recombination route.⁸ Although we favour the biradical mechanism the non-stereospecificity observed in the rearrangement of compound (1) is also consistent with competing concerted-forbidden and allowed suprafacial-inversion rearrangement pathways.⁷

In order both to confirm structure (4) for the rearrangement product of compound (1), and to explain the large value of J_{vic} in this compound, we performed a single-crystal X-ray structure determination of compound (4). The molecular structure is shown in the Figure and bond lengths, bond angles, and torsion angles are given in Table 1. The 8-membered ring has a distorted tub conformation. The steric interaction between the axial substituents at C(5) and C(12) is evident from the abnormally large angles at C(4a) and C(12a) (*ca.* 125°) leading to a transannular non-bonded distance C(5) \cdots C(12) of 316.1 pm, compared with a distance C(6) \cdots C(11) of only 291.5 pm. The torsion angles about the C(5)-C(6) and C(11)-C(12) bonds also

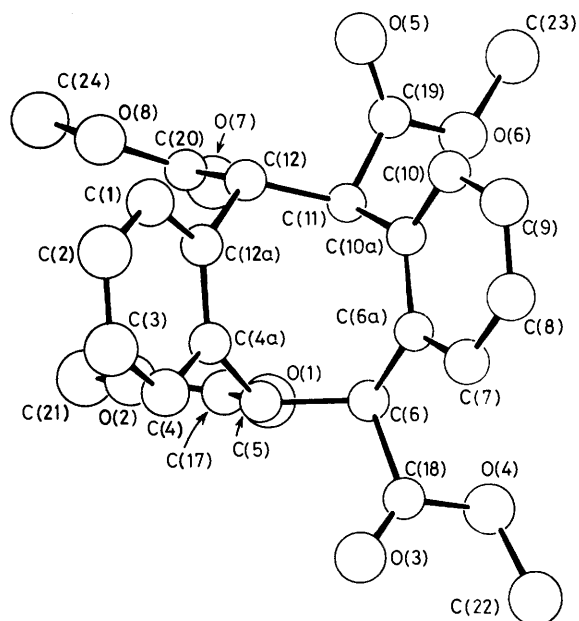


FIGURE Crystal structure of the *trans,trans*-tetrakis(methoxycarbonyl)dibenzo[*a,e*]cyclo-octene (4) with crystallographic numbering scheme

differ greatly from the 'normal' values of 60° and 180°.

The H(5)-C(5)-C(6)-H(6) torsion angle is 119° and that for H(11)-C(11)-C(12)-H(12) is -153°. An averaged J_{vic} value of *ca.* 5 Hz would then be expected for structure (4) if the normal J_{180° value of 9.5 Hz^{9a} is used in the Karplus equation. The observed value

TABLE I

Selected bond lengths (pm) and bond angles (°) with estimated standard deviations in parentheses, and torsion angles (°)

Bond lengths		Bond angles	
C(4a)-C(5)	152.2(4)	C(4a)-C(5)-C(6)	117.9(2)
C(5)-C(6)	156.6(4)	C(5)-C(6)-C(6a)	115.7(2)
C(6)-C(6a)	152.7(4)	C(6)-C(6a)-C(10a)	119.2(2)
C(6a)-C(10a)	140.0(3)	C(6a)-C(10a)-C(11)	120.4(2)
C(10a)-C(11)	152.0(4)	C(10a)-C(11)-C(12)	112.0(2)
C(11)-C(12)	153.8(4)	C(11)-C(12)-C(12a)	117.4(2)
C(12)-C(12a)	152.1(4)	C(12)-C(12a)-C(4a)	125.2(2)
C(12a)-C(4a)	139.9(3)	C(12a)-C(4a)-C(5)	125.6(2)
C-C	137.2-140.0(3)		
(benzene rings)			
C-CO ₂ Me	151.9-152.7(4)		
C=O	119.2-120.2(3)		
C-OMe	132.9-133.5(3)		
O-Me	144.6-145.8(4)		
C-H	86-114(3)		
Torsion angles			
C(12)-C(12a)-C(4a)-C(5)	-1		
C(12a)-C(4a)-C(5)-C(6)	74		
C(4a)-C(5)-C(6)-C(6a)	-8		
C(5)-C(6)-C(6a)-C(10a)	-67		
C(6)-C(6a)-C(10a)-C(11)	4		
C(6a)-C(10a)-C(11)-C(12)	93		
C(10a)-C(11)-C(12)-C(12a)	-37		
C(11)-C(12)-C(12a)-C(4a)	-44		
H(5)-C(5)-C(6)-H(6)	119		
H(11)-C(11)-C(12)-H(12)	-153		

TABLE 2
Atomic co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0.382 2(2)	-0.021 7(2)	0.384 1(2)
C(2)	0.365 4(3)	-0.108 3(2)	0.367 9(2)
C(3)	0.240 6(3)	-0.136 9(2)	0.313 3(2)
C(4)	0.133 3(3)	-0.078 4(2)	0.276 6(2)
C(5)	0.014 0(2)	0.065 8(2)	0.251 4(2)
C(6)	0.047 7(2)	0.125 0(2)	0.177 5(2)
C(7)	0.264 7(2)	0.098 2(2)	0.090 0(2)
C(8)	0.417 2(3)	0.106 1(2)	0.076 5(2)
C(9)	0.524 4(3)	0.144 5(2)	0.136 1(2)
C(10)	0.479 2(2)	0.174 7(2)	0.209 1(2)
C(11)	0.279 4(2)	0.200 5(2)	0.305 1(2)
C(12)	0.305 0(2)	0.132 0(2)	0.374 6(2)
C(4A)	0.145 3(2)	0.009 7(2)	0.293 9(2)
C(6A)	0.216 9(2)	0.129 4(2)	0.162 9(2)
C(10A)	0.326 4(2)	0.168 2(2)	0.223 3(2)
C(12A)	0.273 6(2)	0.038 8(2)	0.349 0(2)
C(17)	-0.077 5(2)	0.113 7(2)	0.310 3(2)
C(18)	-0.056 0(2)	0.098 7(2)	0.097 2(2)
C(19)	0.369 3(2)	0.281 6(2)	0.334 8(2)
C(20)	0.222 8(2)	0.161 3(2)	0.447 3(2)
C(21)	-0.182 9(4)	0.103 6(2)	0.437 3(2)
C(22)	-0.159 4(4)	0.145 5(2)	-0.039 2(2)
C(23)	0.395 5(4)	0.429 9(2)	0.311 5(2)
C(24)	0.194 3(6)	0.136 8(2)	0.588 9(2)
O(1)	-0.141 7(2)	0.180 9(2)	0.295 6(1)
O(2)	-0.086 4(2)	0.067 4(1)	0.379 2(1)
O(3)	-0.111 0(2)	0.028 4(1)	0.083 3(1)
O(4)	-0.077 3(2)	0.164 3(1)	0.043 8(1)
O(5)	0.477 0(2)	0.284 1(1)	0.389 9(1)
O(6)	0.314 8(2)	0.349 9(1)	0.290 4(1)
O(7)	0.141 5(2)	0.223 2(2)	0.445 4(1)
O(8)	0.258 0(2)	0.111 2(1)	0.514 0(1)
H(1)	0.471 5(32)	0.001 9(18)	0.421 6(17)
H(2)	0.438 1(32)	-0.147 7(18)	0.393 8(17)
H(3)	0.228 0(30)	-0.195 5(18)	0.300 9(17)
H(4)	0.048 9(32)	-0.095 0(18)	0.240 0(17)
H(5)	-0.062 3(30)	0.021 6(17)	0.224 9(16)
H(6)	0.015 4(30)	0.186 3(18)	0.187 5(16)
H(7)	0.199 0(30)	0.068 7(17)	0.048 0(17)
H(8)	0.445 9(30)	0.087 2(17)	0.024 1(18)
H(9)	0.628 9(33)	0.151 7(17)	0.125 1(17)
H(10)	0.551 0(32)	0.201 8(18)	0.250 0(17)
H(11)	0.175 9(32)	0.219 0(17)	0.297 7(17)
H(12)	0.413 5(32)	0.135 7(17)	0.398 6(16)
H(21A)	-0.137 7(33)	0.156 2(18)	0.464 4(18)
H(21B)	-0.283 7(33)	0.101 2(18)	0.414 0(18)
H(21C)	-0.184 4(32)	0.060 0(18)	0.475 6(18)
H(22A)	-0.108 5(30)	0.086 1(18)	-0.065 9(17)
H(22B)	-0.150 6(32)	0.190 4(18)	-0.075 4(18)
H(22C)	-0.251 4(33)	0.121 6(18)	-0.035 4(18)
H(23A)	0.359 1(30)	0.466 0(18)	0.268 0(18)
H(23B)	0.361 1(30)	0.451 2(18)	0.361 8(18)
H(23C)	0.506 6(34)	0.419 3(18)	0.310 8(17)
H(24A)	0.214 8(34)	0.192 8(18)	0.599 4(18)
H(24B)	0.085 7(33)	0.151 8(18)	0.576 2(18)
H(24C)	0.235 9(33)	0.102 2(18)	0.627 4(18)

J_{vic} (8 Hz) requires a J_{180° value of *ca.* 16 Hz which is one of the largest known diaxial coupling constants in cyclohexanes.^{9b} This factor, and the distortion of the geometry of compound (4) associated with relief of steric repulsion between the C(5) and C(12) methoxy-carbonyl groups, account for the original, erroneous assignment of stereochemistry to compound (4).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified, i.r. spectra refer to Nujol mulls and ¹H n.m.r. spectra refer to solutions in CDCl₃ measured with a Perkin-Elmer R32 spectrometer (90 MHz). ¹³C

n.m.r. spectra were determined on a Jeol FX90Q spectrometer. Low-resolution mass spectra were obtained with a Kratos MS25 instrument, and accurate mass measurements were made using a Kratos MS9/50 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by t.l.c. in more than one solvent system as well as by n.m.r. measurements and crystallisation to constant m.p. Chromatography (on silica) refers to short-column chromatography¹⁰ over Kieselgel G (Merck).

The Spiro-dimer (1) of α,α' -Bis(methoxycarbonyl)-o-quinodimethane.—Dimethyl α,α' -dibromo-*o*-phenylenediacetate (5.7 g), dimethylformamide (60 ml), and sodium iodide (13.5 g) were stirred under nitrogen during 18 h. The product was diluted with water and extracted into dichloromethane, and the extract was washed with aqueous sodium thiosulphate and then with water, dried (MgSO₄), and evaporated to dryness. The product was triturated with diethyl ether to give the previously described spiro-dimer (2.16 g), m.p. 160–162 °C (lit.,¹ 158–158.5 °C). Recrystallisation from ethanol with the aid of dichloromethane did not raise the m.p. of this product; δ 3.56 (3 H, s, OMe), 3.60 (3 H, s, OMe), 3.68 (3 H, s, OMe), 3.79 (1 H, s, HD), 3.80 (3 H, s, OMe), 4.35 (1 H, d, *J* 11 Hz, HB), 4.53 (1 H, d, *J* 11 Hz, HC), 5.75–6.36 (4 H, m, olefinic H), 6.95–7.46 (4 H, m, aromatic), and 7.75 br (1 H, d, *J* 9 Hz, HA). Irradiation of the multiplet at δ 6.22 caused the collapse of the resonance at δ 7.75 to a broad singlet. The singlet at δ 3.79 in CDCl₃ solution was clearly observed at δ 3.97 in C₆D₆ solution in which the methoxy-group protons appeared at δ 3.33–3.54. δ_C 45.43, 47.82, 51.09, 51.95 (2 lines), 52.115, 52.765, 57.42, 115.50, 122.81, 123.14, 127.797 (2 lines), 128.34, 128.72, 129.48, 131.16, 131.75, 134.352, 154.45, 165.94, 170.38, 172.38, and 172.76 p.p.m.; ν_{max} 1 735 m, 1 715, and 1 645 cm⁻¹.

1,2,3,4-Tetrahydro-1,2,3,4-tetrakis(methoxycarbonyl)-naphthalene.—Dimethyl α,α' -dibromo-*o*-phenylenediacetate (0.475 g), dimethyl fumarate (0.36 g), methanol (5 ml), and sodium iodide (1.25 g) were stirred under nitrogen during 24 h. The product was diluted with water and extracted with diethyl ether. The extract was washed with aqueous sodium thiosulphate and then with water, dried (MgSO₄), and evaporated to dryness to give a crude product which was purified by chromatography [benzene–diethyl ether (4 : 1) as eluant] and crystallisation from ethanol to give the *title compound*, m.p. 79–83 °C (Found: *M*⁺, 364.116. C₁₈H₂₀O₈ requires *M*, 364.116); δ 7.1–7.4 (4 H, m, aromatic), 3.8 (total 9 H, s, 3 × OMe), 3.7 (3 H, s, OMe), and 3.0–4.5 (4 H, complex m, 4 × CHCO₂Me); δ_C 174.39, 172.60, 171.895, 171.35, 131.89, 131.59, 130.07, 128.39 (2 lines), 127.635, 53.00, 52.66, 52.39 (2 lines), 48.81, 46.10, 43.12, and 41.12 p.p.m.

The ¹³C n.m.r. spectrum of the previously prepared ¹*N*-phenylmaleimide adduct (5) of α,α' -bis(methoxycarbonyl)-*o*-quinodimethane was also recorded: δ_C [CH₂Cl₂–(CH₃)₂CO] 176.23, 171.03, 134.03, 133.43, 131.05, 129.37, 128.88 (2 lines), 127.31, 45.885, 42.039; the methoxy-group resonances were obscured by the solvent.

Photochemical Isomerisation of the Spiro-dimer (1).—A solution of the spiro-dimer (1) (300 mg) in acetonitrile (15 ml) in a quartz flask was boiled under reflux under argon to remove oxygen. After being cooled the solution was irradiated by placing the flask close to the water-cooled jacket of a 1 kW medium-pressure mercury lamp. The progress of the reaction was followed by n.m.r. examination

of aliquots withdrawn at intervals. After 135 min very little starting material remained and the solution was evaporated to dryness and the product was chromatographed on silica (140 g) with benzene-diethyl ether (9:1) as eluant to give, first, *r*-5,*c*-6,*c*-11,*t*-12-5,6,11,12-tetrahydro-5,6,11,12-tetrakis(methoxycarbonyl)dibenzo[a,e]cyclo-octene (7) (30 mg), m.p. 188–191 °C (from ethanol) (Found: C, 65.5; H, 5.35. $C_{24}H_{24}O_8$ requires C, 65.45; H, 5.45%); ν_{\max} . 1740 cm^{-1} ; δ 3.65 (3 H, s), 3.72 (3 H, s), 3.75 (3 H, s), 3.85 (3 H, s), 4.4 (1 H, d, *J* 11 Hz), 4.82 (1 H, d, *J* 11 Hz), 4.97 (2 H, two strong inner lines of AB system), 6.56 (1 H, m), 6.76–7.2 (6 H, m), and 7.6br (1 H, d, *J* 7 Hz). The coupling constant associated with the second AB system could be measured (9 Hz) by addition of a few drops of benzene to the $CDCl_3$ solution. The similar spectrum for these protons observed in chlorobenzene showed no change in appearance at 115 °C.

Further elution gave (E)-3',4'-dihydro-1',3',4'-tris-(methoxycarbonyl)-6-methoxycarbonylmethylenespiro[cyclohexa-2,4-diene-1,2'-(1'-H)-naphthalene] (6a) (160 mg), m.p. 170–172 °C (from ethanol) (Found: C, 65.7; H, 5.65. $C_{24}H_{24}O_8$ requires C, 65.45; H, 5.45%), ν_{\max} . 1580, 1705, 1723, 1740, and 1755 cm^{-1} ; δ 3.44 (1 H, d, *J* 9 Hz), 3.54 (3 H, s), 3.66 (3 H, s), 3.75 (6 H, s), 4.42br (1 H, s), 4.54br (1 H, d, *J* 9 Hz), 5.55–5.84 (1 H, m, olefinic), 5.95–6.3 (3 H, m, olefinic), 6.82–7.0 (1 H, m, aromatic), 7.0–7.53 (3 H, m, aromatic), and 7.68–7.93 (1 H, m, H^A). Irradiation of the olefinic multiplet at δ 5.95–6.3 caused the collapse of the signal at δ 7.68–7.93 to a broad singlet, and irradiation of the doublet at δ 3.44 caused the doublet at δ 4.54 to collapse to a singlet. δ_C 46.21 (2 lines), 51.19, 52.01, 52.22, 52.765, 57.53, 59.27, 115.61, 123.41, 124.44, 127.97 (4 lines), 128.23, 131.10, 131.75, 132.02, 156.83, 166.37, 170.92 (2 lines), and 173.09 p.p.m.

Continued elution gave the (Z)-isomer (6b) (170 mg), m.p. 176–179 °C (from diethyl ether) (Found: M^+ , 440.147. $C_{24}H_{24}O_8$ requires M , 440.147); ν_{\max} . 1560, 1593, 1656, 1736, and 1753 cm^{-1} ; δ 3.58 (3 H, s), 3.64 (3 H, s), 3.72 (3 H, s), 3.78 (3 H, s), 4.47br (1 H, d, *J* 10 Hz), 5.06 (1 H, d, *J* 10 Hz), 5.58br (1 H, s), 5.64–5.88 (1 H, m, olefinic), 5.88–6.26 (4 H, m, olefinic), 6.98 (1 H, m, aromatic), and 7.12–7.53 (3 H, m, aromatic). Irradiation of the broad singlet at δ 5.58 sharpened the doublet at δ 4.47. With iodine (20 mg) in boiling benzene (3 ml) compound (6b) (40 mg) was completely converted into its isomer (6a) (2 h).

Addition of 4-Phenyl-4H-1,2,4-triazole-3,5-dione to the Spiro-compounds (1), (6a), and (6b).—*Typical method.* The dienophile (5 mg) and the spiro-compound (6a) (11 mg) were dissolved in $CDCl_3$ (0.25 ml) and the progress of the reaction was followed by n.m.r. spectroscopy. Reaction was rapid, being essentially complete after 30 min. Evaporation of the solution and crystallisation of the residue from ethanol gave the adduct of compound (6a), m.p. 225–230 °C (Found: M^+ , 615.186. $C_{32}H_{29}N_3O_{10}$ requires M , 615.185); ν_{\max} . 1654, 1720, 1730, and 1780 cm^{-1} ; δ 3.03 (1 H, d, *J* 12 Hz), 3.61 (3 H, s), 3.64 (3 H, s), 3.67 (3 H, s), 3.85 (3 H, s), 4.04 (1 H, s), 5.19 (1 H, s), 5.19 (1 H, d, *J* 12 Hz), 5.94 (1 H, dd, *J* 6 and 2 Hz), 6.49 (2 H, m), 7.08 (1 H, dd, *J* 6 and 2 Hz), and 7.2–7.9 (9 H, m). Irradiation of the doublet at δ 3.03 caused the collapse of the doublet at δ 5.19 to a singlet.

The adduct from spiro-compound (1) was similarly prepared in benzene, m.p. 210–220 °C (from ethanol) (Found: M^+ , 615.185); ν_{\max} . 1662, 1710, 1720, 1730, and 1780

cm^{-1} ; δ 3.55 (3 H, s), 3.70 (3 H, s), 3.80 (6 H, s), 4.40 (1 H, s), 4.57 (1 H, dd, *J* 5 and 3 Hz), 4.66 (2 H, coincident inner lines of AB system), 6.14 (1 H, s), 6.39 (2 H, m, $CH=CH$), 6.90 (1 H, dd, *J* 5 and 3 Hz), and 7.1–8.0 (9 H, m).

The adduct from spiro-compound (6b) was similarly prepared in benzene during 18 h, m.p. 289–290 °C (from ethanol) (Found: M^+ , 615.184); ν_{\max} . 1662, 1715, 1725, and 1779 cm^{-1} ; δ 3.60 (6 H, s), 3.79 (6 H, s), 4.67br (1 H, d, *J* 13 Hz), 4.85 (1 H, d, *J* 13 Hz), 5.15 (2 H, m), 5.70br (1 H, s), 6.25–6.55 (3 H, m), and 6.95–7.70 (9 H, m).

Thermolysis of the Spiro-compounds (1), (6a), and (6b).—*Typical method.* The spiro-compound (1) (100 mg) and xylene (4 ml) were heated under reflux under nitrogen during 20 h. Evaporation of the solvent and crystallisation of the residue from ethanol gave the known compound (4) (75 mg), m.p. 253–256 °C (lit.¹ 255–255.5 °C); ν_{\max} . 1714 and 1730 cm^{-1} ; δ (60 MHz) 3.6 (6 H, s), 3.78 (6 H, s), 4.68 (2 H, d, *J* 8 Hz), 5.08 (2 H, d, *J* 8 Hz), and 6.6–7.3 (8 H, m). The 90 MHz spectrum run at 35 °C in a mixture of *o*-dichlorobenzene, $[^2H_5]$ pyridine, and $[^2H_6]$ dimethyl sulphoxide showed an AB system at δ 4.88 and 5.27 which collapsed to a broad singlet (δ 5.0) at 116 ± 4 °C. At the same time the methoxy-group singlets (δ 3.42 and 3.55) at 35 °C collapsed to a singlet (δ 3.5) at 116 ± 4 °C. The crystal employed in the X-ray analysis of this compound (see below) was obtained by recrystallisation from benzene.

The ethanolic mother liquor from the crystallisation of compound (4) was evaporated to dryness and the residue was chromatographed [benzene-diethyl ether (9:1) as eluant]. Elution of the column gave, first, a further crop of compound (4) (4 mg) and then the isomeric dibenzocyclo-octene (7) (15 mg), identical with the sample previously prepared (n.m.r.). Both compounds (4) and (7) were recovered unchanged after being heated in boiling xylene (5 h).

Similarly, the spiro-compound (6a) (10 mg) and xylene (3 ml) were heated under reflux under nitrogen during 2 h. The mixture was evaporated to dryness and the n.m.r. spectrum of the residue indicated the presence of a trace of spiro-compound (6a) and the dibenzocyclo-octene (7) as the major product.

Similarly, the spiro-compound (6b) (10 mg) and xylene (3 ml) were heated under reflux under nitrogen during 8 h. Evaporation of the solvent gave the pure dibenzocyclo-octene (2), m.p. 235–237 °C (from ethanol) (Found: C, 65.5; H, 5.6%; M^+ , 440.147. $C_{24}H_{24}O_8$ requires C, 65.45; H, 5.45%; M , 440.147); ν_{\max} . 1735 cm^{-1} ; δ 3.73 and 3.74 (total 12 H, two lines, 4 OMe), 4.46 (2 H, d, *J* 12 Hz), 5.19 (2 H, d, *J* 12 Hz), and 6.8–7.5 (8 H, m, aromatic).

Reaction of Spiro-compound (1) with Boron Trifluoride-Diethyl Ether in Benzene.—The spiro-compound (1) (300 mg), benzene (6 ml), and boron trifluoride-diethyl ether (280 mg) were heated under reflux under nitrogen during 16 h. The product was diluted with diethyl ether and the solution was washed with aqueous sodium hydrogen carbonate and then with water, dried ($MgSO_4$), evaporated to dryness, and the residue was chromatographed [benzene-diethyl ether (4:1) as eluant] to give, in order of elution, (a) compound (12) (80 mg), m.p. 111–113 °C (from ethanol) (Found: M^+ , 518.194. $C_{30}H_{30}O_8$ requires M , 518.194); ν_{\max} . 1730 and 1740 cm^{-1} ; δ 3.45 (3 H, s), 3.59 (3 H, s), 3.67 (3 H, s), 3.68 (3 H, s), 3.45–3.68 (2 H, obscured m, CH_2), 3.76 (2 H, coincident strong inner lines of AB system), 5.20 (1 H, s), and 7.0–7.6 (13 H, m); (b) the dibenzocycloheptene (8a) (80 mg), m.p. 145–146 °C (from ethanol)

(Found: M^+ , 440.147. $C_{24}H_{24}O_8$ requires M , 440.147); ν_{\max} . 1725 and 1730 cm^{-1} ; δ 3.52 (3 H, s), 3.61 (3 H, s), 3.71 (6 H, s), 3.5—3.7 (2 H, obscured m, CH_2), 4.74 (1 H, d, J 8 Hz), 5.01 (1 H, d, J 8 Hz), 5.26 (1 H, s), 7.0—7.44 (6 H, m), and 7.44—7.66 (1 H, m). In the presence of ca. 25% benzene the signals in the δ 3.5—3.7 region appear as 3H-singlets at δ 3.35, 3.48, 3.54, and 3.56, and the CH_2 group appears as an apparent singlet at δ 3.65. The mass spectrum includes strong peaks at m/z 408, 381, 349, 321, 289, 263, 231, 203, and 202 (100, 29.4, 10.4, 81.3, 17.0, 34.3, 13.0, 58.3, and 59.1%, respectively); and (c) one of the epimeric lactones (11) (40 mg), m.p. 166—169 °C (from ethanol) (Found: M^+ , 426.131. $C_{23}H_{22}O_8$ requires M , 426.131); ν_{\max} . 1734, 1740, 1750, and 1760 cm^{-1} ; δ 3.2 (1 H, d, J 16.5 Hz), 3.25 (1 H, d, J 16.5 Hz), 3.52 (3 H, s), 3.76 (3 H, s), 3.9 (3 H, s), 3.53 (2 H, coincident strong inner lines of AB system), 5.93 (1 H, s), 6.26br (1 H, d, J 8 Hz, aromatic), 6.8—7.5 (6 H, m, aromatic), and 7.86br (1 H, d, J 8 Hz, aromatic). The mass spectrum included strong peaks at m/z 362, 247, 221, 202, 161, and 118 (12.0, 11.7, 100, 11.9, 56.5, and 27.6%, respectively).

Reaction of Spiro-compound (6a) with Boron Trifluoride-Diethyl Ether in Benzene.—The spiro-compound (6a) (100 mg), benzene (6 ml), and boron trifluoride-diethyl ether (234 mg) were heated under reflux under nitrogen during 3 h. After work-up as described in the preceding experiment, the product was chromatographed [benzene-diethyl ether (4 : 1) as eluant] to give, first, one of the epimeric lactones (11) (45 mg), m.p. 150—154 °C (from ethanol) (Found: M^+ , 426.131); δ 3.60 (1 H, d, J 16.5 Hz), 3.63 (3 H, s), 3.69 (3 H, s), 3.86 (3 H, s), 4.24 (1 H, d, J 16.5 Hz), 4.69 (1 H, d, J 10 Hz), 5.09br (1 H, d, J 10 Hz), 5.76 (1 H, s), 6.7—7.0 (1 H, m, aromatic), and 7.0—7.5 (7 H, m, aromatic). The mass spectrum included strong peaks at m/z 362, 247, 221, 202, 161, 119, and 118 (15.2, 14.2, 100, 19.2, 60.6, 32.5, and 27.1%, respectively).

Continued elution gave the dibenzocycloheptene (8b) (50 mg), m.p. 178—180 °C (from ethanol) (Found: M^+ , 440.147. $C_{24}H_{24}O_8$ requires M , 440.147); ν_{\max} . 1725, 1740, and 1750 cm^{-1} ; δ 3.62 (6 H, s), 3.70 (3 H, s), 3.75 (3 H, s), 3.94 (1 H, d, J 16 Hz), 3.62—3.75 obscured (1 H, d, J 16 Hz) [the strong inner line of this signal is observed at δ 3.7 on addition of a few drops of benzene to the $CDCl_3$ solution], 4.7 (1 H, d, J 9 Hz), 4.8 (1 H, s), 5.08 (1 H, d, J 9 Hz), 6.86—7.10 (1 H, m), and 7.1—7.4 (6 H, m). The mass spectrum includes strong peaks at m/z 408, 381, 349, 321, 289, 263, 231, 203, and 202 (100, 33.2, 12.4, 76.7, 24.2, 34.1, 12.3, 57.0, and 53.1%, respectively).

*Reaction of Spiro-compound (1) with Toluene-*p*-sulphonic Acid.*—The spiro-compound (1) (100 mg), benzene (5 ml), and toluene-*p*-sulphonic acid (50 mg) were heated under reflux during 4 h. The product was diluted with diethyl ether and the solution was washed in turn with saturated aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to dryness. The crude residue was crystallised from diethyl ether to give one of the epimeric tosylates (9) (80 mg), m.p. 140—142 °C (from $CH_2Cl_2-Et_2O$) (Found: M^+ , 612.166. $C_{31}H_{32}SO_{11}$ requires M , 612.166); ν_{\max} . 1730 cm^{-1} ; δ 2.48 (3 H, s), 3.54 (2 H, coincident strong inner lines of AB system), 3.56 (3 H, s), 3.62 (3 H, s), 3.69 (6 H, s, 2 \times OMe), 4.76 (1 H, d, J 10 Hz), 4.91 (1 H, d, J 10 Hz), 6.15 (1 H, s), 7.0—7.6 (10 H, m), and 7.88br (2 H, d, J 8 Hz).

Evaporation of the mother liquor from the crystallisation of compound (9) gave a mixture (60 mg) which was chromatog-

raphed [benzene-diethyl ether (4 : 1) as eluant] to give, in order of elution, (a) recovered starting material (15 mg), (b) a further quantity (10 mg) of the aforementioned epimer of tosylate (9), and (c) the dibenzocycloheptene (8a) (15 mg). The n.m.r. spectra of fractions (b) and (c) indicated the presence of traces of the epimer of the tosylate (9) obtained below by reaction of the spiro-compound (6a) with toluene-*p*-sulphonic acid.

*Reaction of Spiro-compound (6a) with Toluene-*p*-sulphonic Acid.*—The spiro-compound (6a) (35 mg), toluene-*p*-sulphonic acid (25 mg), and benzene (3 ml) were heated under reflux during 15 h. The product was worked up as described in the preceding experiment. Chromatography [benzene-diethyl ether (4 : 1) as eluant] gave, first, a second epimer of the tosylate (9) (15 mg), m.p. 126—132 °C (from diethyl ether) (Found: C, 62.0; H, 5.3%; M^+ , 612.165. $C_{31}H_{32}SO_{11}$ requires C, 60.8; H, 5.3%; M , 612.166); ν_{\max} . 1730 and 1740 cm^{-1} ; δ 2.44 (3 H, s), 3.60 (3 H, s), 3.67 (6 H, s), 3.70 (3 H, s), 3.60—3.70 obscured (2 H of AB system), 4.81 (1 H, d, J 11 Hz), 5.0 (1 H, d, J 11 Hz), 6.36 (1 H, s), 7.0—7.5 (10 H, m), and 7.79br (2 H, d, J 9 Hz).

Continued elution gave the dibenzocycloheptene (8b) (15 mg) identical (n.m.r.) with the material obtained earlier. The n.m.r. spectrum of the tosylate fractions obtained from the aforementioned chromatography indicated the presence of traces of the epimer of the tosylate (9) obtained earlier from the spiro-compound (1), as well as traces of the lactone (11) obtained earlier by reaction of the spiro-compound (6a) with boron trifluoride-diethyl ether.

Hydrogenolysis of the Epimeric Tosylates (9).—The epimeric tosylate (9) [obtained from the spiro-compound (1)] (40 mg), 10% palladium-charcoal (10 mg), and ethyl acetate (4 ml) were shaken under hydrogen during 17 h. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was dissolved in dichloromethane and washed in turn with saturated aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to give α,α' -bis(methoxycarbonyl)-2,2'-bis(methoxycarbonylmethyl)biphenyl (10) (25 mg), m.p. 133 and 138—139 °C (from ethanol) (Found: M^+ , 442.1635. $C_{24}H_{26}O_8$ requires M , 442.163); ν_{\max} . 1730 cm^{-1} ; δ 3.12 (2 H, d, J 16 Hz), 3.38 (2 H, d, J 16 Hz), 3.62 (12 H, s), 4.58 (2 H, s), 6.85—7.25 (6 H, m), and 7.25—7.50 (2 H, m). Hydrogenolysis of the epimeric tosylate (9), obtained from the spiro-compound (6a), was conducted in the same way and gave the same product (10) (identical by i.r. and n.m.r.).

Crystal Data of Compound (4).— $C_{24}H_{24}O_8$, $M = 440.43$, monoclinic, $a = 0.871$ 2(2), $b = 1.554$ 4(3), $c = 1.612$ 2(3) nm, $\beta = 98.19$ (2)°, $U = 2.161$ 0(6) nm³, $Z = 4$, $D_c = 1.354$ Mg m⁻³, $F(000) = 928$, space group $P2_1/c$. Mo- K_α radiation, $\lambda = 71.069$ pm.

Structure Determination.—Measurements were made on a Syntex P2₁ diffractometer. Cell dimensions were determined by least-squares treatment on the setting angles of 15 reflections having $35 < 2\theta < 40^\circ$. All independent reflections to $2\theta = 45^\circ$ were measured in the θ - 2θ scan mode, and the structure analysis used the 2376 reflections having $I > 3\sigma(I)$. Computations were carried out using the SHELX76 program. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic vibration parameters for carbon and oxygen atoms. A difference synthesis then gave the positions of all hydrogen atoms. These were included in the refinement with fixed isotropic temperature factors of $U = 500$ pm². Refinement then converged to final values $R = R' = 0.041$.

Least-squares weights were calculated from counting statistics. The final atomic co-ordinates and their estimated standard deviations are given in Table 2. The anisotropic vibration parameters and a list of observed and calculated structure factors are in Supplementary Publication No. SUP 23362 (16 pp.).*

* For details, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. I*, 1981, Index issue.

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