however, excepting the generally longer *relative* relaxation times for apical boron nuclei (regardless of chemical shift), we caution against spectral and structural assignments by this method.

Since B(2,2′) and B(4,4′) have different T_1 values, it is impossible to obtain a PRFT spectrum in which both are nulled and the resonances from B(3,3′,5,5′) are clearly resolved. However, the B(3,3′,5,5′) doublet (Figure 3C) may be easily generated by digitally subtracting the PRFT spectrum containing only B(2,2′) and B(4,4′) (Figure 3B) from the normal spectrum containing all three resonances (Figure 3A). Computer simulation[14] of the low-field resonances generated from peaks of 90 Hz width shows that the doublet of intensity 4 must be the doublet at δ +10.7 ppm in order to reconstruct the normal spectrum, thus confirming our assignment.

The strength of the partially relaxed Fourier transform technique rests in the fact that it obtains increased spectral resolution *not* from chemical shift differences or high magnetic field strengths but from the inherent relative differences in spin–lattice relaxation times of the various types of nuclei in the molecule itself.

Acknowledgments. The authors gratefully note the support of the National Science Foundation (Grant No. GP-24266x). Professor Adam Allerhand, Mr. A. O. Clouse, and Mr. T. Roseberry are acknowledged for the design, building, and operation of the equipment necessary to observe PRFT spectra. Professor Allerhand is also thanked for many useful discussions.

(14) Software modified from NMRCAL, Nicolet Instrument Corp., Madison, Wis.

Diastereomeric Monocyclic Diallenes. Synthesis and Properties of the Diastereomeric 3,4,9,10-Cyclododecatetraene-1,7-diones and 3,4,10,11-Cyclotetradecatetraene-1,8-diones[1]

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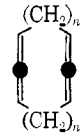
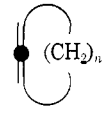
Contribution from the Department of Chemistry, University College London, London WC1H OAJ, England. *Received September 29, 1972*

Abstract: Reaction of 4,4,9,9-tetramethoxycyclododeca-1,6-diene (**3**) with bromoform and potassium *tert*-butoxide gave 6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**4**), predominantly as the anti isomer. Treatment of **4** with methyllithium at −10° gave a mixture of the diastereomeric racemic (**5a**) and meso (**5b**) 5,5,11,11-tetramethoxy-1,2,7,8-cyclododecatetraenes, which on hydrolysis gave the corresponding racemic (**6a**) and meso (**6b**) 3,4,9,10-cyclododecatetraene-1,7-diones. A partial asymmetric synthesis of **5a, 5b** using methyllithium in the presence of (−)-sparteine gave an optically active sample of **5a**, and allowed the identification of the racemic and meso isomers. The composition of the diketal mixture **5a, 5b** was shown to be the same whether derived from the anti or syn tetrabromide (**4a** or **4b**) as a precursor. The diketal **5** rearranged with methyllithium at 35° to give 5,5,11,11-tetramethoxy-2,7-tricyclo[7.3.0.0^{2,7}]dodecadiene (**13**). Reaction of **5** with sodium in liquid ammonia gave a mixture of products, from which *cis,cis*-4,4,10,10-tetramethoxy-1,7-cyclododecadiene (**21**) was obtained. Reaction of **21** with bromoform and potassium *tert*-butoxide gave 7,7,14,14-tetrabromo-3,3,10,10-tetramethoxytricyclo[11.1.0.0^{6,8}]tetradecane (**24**), which, on treatment with methyllithium at −10°, gave a mixture of the diastereomeric racemic (**25a**) and meso (**25b**) 5,5,12,12-tetramethoxy-1,2,8,9-cyclotetradecatetraenes. Hydrolysis of **25a** and **25b** gave the corresponding racemic (**26a**) and meso (**26b**) 3,4,10,11-cyclotetradecatetraene-1,8-diones, these compounds again being identified through a partial asymmetric synthesis.

The preparation of cyclic allenes by treatment of the corresponding dibromocyclopropane derivatives with methyllithium has been studied by Skattebøl[2] and Moore and Ward.[3] Skattebøl[2] prepared two monocyclic diallenes, 1,2,6,7-cyclodecatetraene (**1**, n = 2) and 1,2,9,10-cyclohexadecatetraene (**1**, n = 5), by this route, as low melting, crystalline solids. Both of these diallenes possess two chiral centers and should



1, n = 2
n = 5



2, n = 6
n = 7
n = 8

exist in two diasteromeric forms, one diastereomer being racemic and the other a meso compound. However, no separation of the diastereomeric forms was reported. Moore and Ward[3] prepared 1,2-cyclononadiene (**2**, n = 6), 1,2-cyclodecadiene (**2**, n = 7), and 1,2-cycloundecadiene (**2**, n = 8) by the same type of reaction. The properties of 1,2-cyclononadiene have been extensively investigated, and both a partial reso-

(1) For preliminary communications of part of this work, see P. J. Garratt, K. C, Nicolaou, and F. Sondheimer, *Chem. Commun.*, 1219 (1970); R. Baker, P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Tetrahedron Lett.*, 3425 (1972).

(2) L. Skattebøl, *Tetrahedron Lett.*, 1967 (1961); *Acta Chem. Scand.*, 17, 1683 (1963).

(3) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); 27, 4179 (1962).

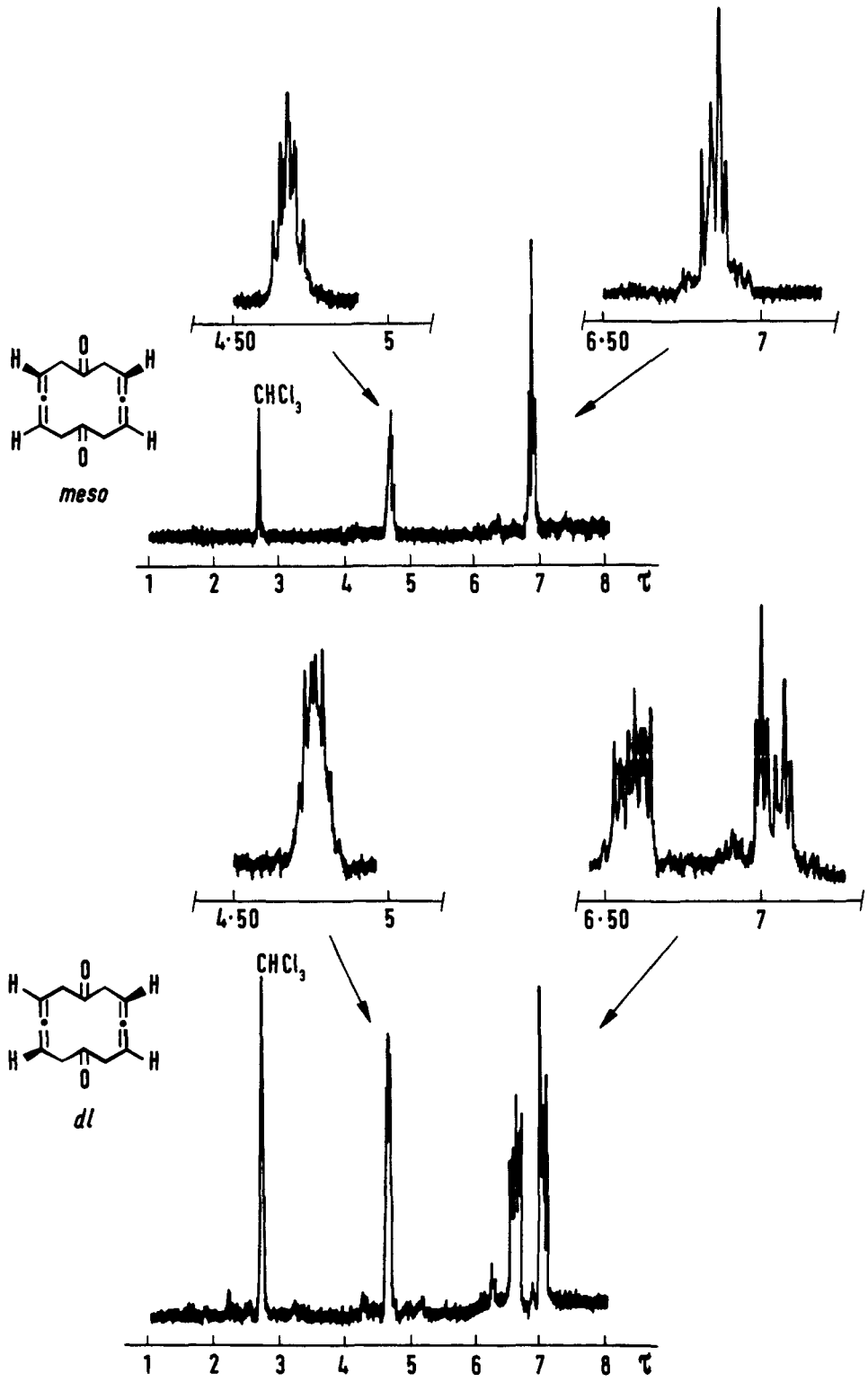


Figure 1. Nmr spectra (220 MHz) of racemic (**6a**) and meso (**6b**) 3,4,9,10-cyclododecatetraene-1,7-diones in $CDCl_3$ with TMS as internal standard.

lution and an asymmetric synthesis have been achieved,[4] the pure isomer having an estimated $[\alpha]_D$ of *ca.* 170–175° in CH_2Cl_2. These latter observations suggested that not only should it be possible to prepare diastereomers of monocyclic diallenes, but that it should also be possible to distinguish between the racemic and meso stereomers by either resolution or asymmetric synthesis. Consequently, we undertook an examination of the preparation of diastereomeric monocyclic diallenes. As we were also interested in such systems containing other functional groups, we have investigated the ring expansion of 4,4,9,9-tetramethoxy-1,6-cyclodecadiene (**3**) *via* the dibromocarbene route. We now report the synthesis and separation of the diastereomeric diallenes, 3,4,9,10-cyclododecatetraene-1,7-dione (**6**) and 3,4,10,11-cyclotetradecatetraene-1,8-

(4) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **92**, 1243 (1970).

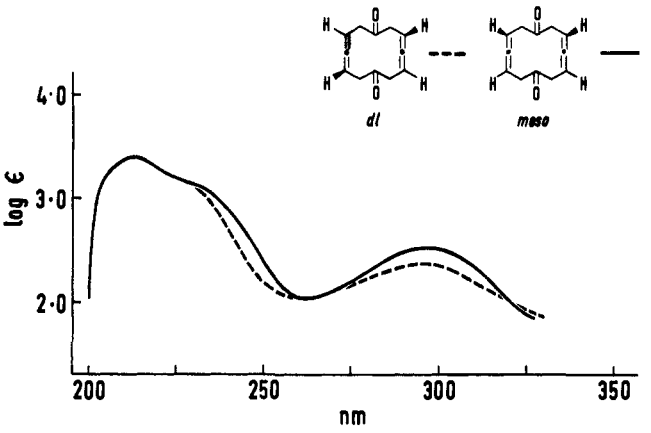


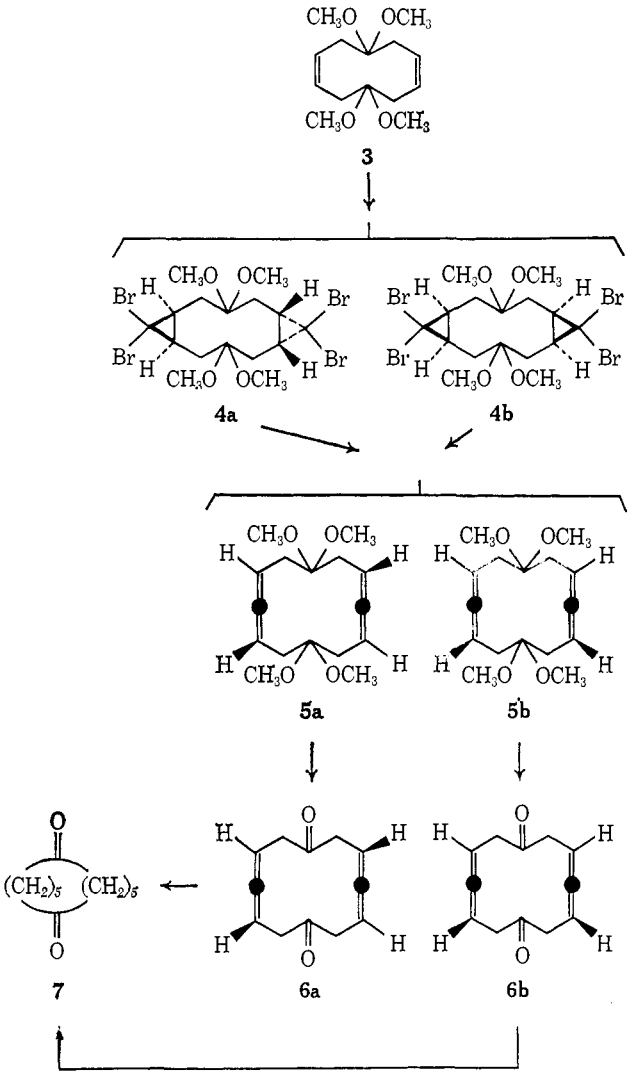
Figure 2. Electronic spectra of racemic (**6a**) and meso (**6b**) 3,4,9,10-cyclododecatetraene-1,7-diones in ethanol.

dione (**26**), and the identification of the racemic and meso forms.

The diketal **3**, prepared by the method of Grob and Schiess,[5] was treated with excess bromoform and potassium *tert*-butoxide in pentane at 0°. The major product (80%) precipitated as an amorphous powder. After slow crystallization from CH_2Cl_2 it was identified as *anti*-6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**4a**), mp 155–156°. The nmr spectrum showed only one methoxyl signal, suggesting the anti rather than the syn stereochemistry, and the stereochemical assignment was confirmed by a full X-ray crystallographic analysis.[6] The pentane solution remaining after the removal of **4a** was found to contain the corresponding mono(dibromocarbene) adduct,[7] together with about 1% of *syn*-6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**4b**), mp 148–149°. The nmr spectrum of **4b** showed two methoxyl signals, and the syn stereochemistry is supported by a partial X-ray crystallographic analysis.[8]

Treatment of either isomer **4a** or **4b** with methyllithium in ether at −10° led to 80% of a diastereomeric mixture (1:2) of racemic (**5a**) and meso (**5b**) 5,5,11,11-tetramethoxy-1,2,7,8-cyclododecatetraene, which could be separated by chromatography (Scheme I). The gross structures of **5a**, mp 116–118°, and **5b**, mp 86–87.5°, are based on the spectral and chemical properties and the stereochemical assignments are based on a partial asymmetric synthesis. The nmr spectra of **5a** and **5b** are consistent with the monocyclic diallene structure, and the ir spectra (ν 1960 cm^{-1}) confirmed the presence of an allene group. Hydrolysis of **5a** with dilute sulfuric acid in ether gave the corresponding dione **6a**, mp 96–97°, and similar hydrolysis of **5b** gave the corresponding dione **6b**, mp 67–68°. The spectral properties of **6a** and **6b** [ir (KBr) 1960 (allene) and 1710 cm^{-1} (ketone); nmr 220 MHz (Figure 1)] were consistent with the gross structural assignments, and hydrogenation of either isomer in ethyl acetate over platinum gave cyclododecane-1,7-dione (**7**), mp 134–135° (lit.[9] 134–136°).

Scheme I



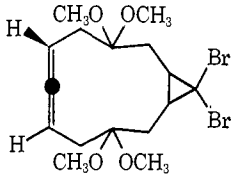
Reaction of **4a** with methyllithium at −10° in the presence of (−)-sparteine[10] gave the diastereomeric mixture of **5a** and **5b**, which was again separated. The compound, mp 113–116°, was found to be optically active ([α]^{20}D +24.45 ± 0.05°) and in consequence corresponds to the racemic isomer **5a**; whereas the compound, mp 86–87.5°, showed no optical activity and must be the meso isomer **5b**. Hydrolysis of **5a** with dilute sulfuric acid gave optically active diones **6a** ([α]^{20}D +55.55 ± 0.05°), while hydrolysis of **5b** gave the inactive meso dione **6b**. The identities of the racemic and meso forms of 3,4,9,10-cyclododecatetraene-1,7-dione are thus established.

The electronic spectra of **6a** and **6b** showed, besides the absorption bands at ~230 nm due to the allene chromophore, low intensity maxima at longer wavelength [**6a**, 295 nm (ϵ 270); **6b**, 296 nm (ϵ 370), Figure 2]. These latter absorption bands are presumably due to a photodesmotic n → π^* transition, similar to that observed in 3,8-cyclodecadiene-1,6-dione and related systems.[5,11]

(5) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960).
(6) R. Baker and P. J. Pauling, *J. Chem. Soc., Perkin Trans. 2*, 1451 (1972).
(7) P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *J. Org. Chem.*, **38**, 864 (1973).
(8) R. Baker and P. J. Pauling, unpublished results.
(9) Upjohn Co., British Patent 1,036,084 (1966); *Chem. Abstr.*, **65**, 11307*h* (1966).
(10) H. Nozaki, T. Aratami, T. Toraya, and R. Noyari, *Tetrahedron*, **27**, 905 (1971).
(11) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); J. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); E. Kosower, W. D. Closson, H. L. Goering, and J. C. Cross, *J. Amer.*

Comparison of the nmr spectra (220 MHz, Figure 1) of **6a** and **6b** reveals that the racemic isomer **6a** shows two regions of absorption for the methylene protons, whereas the meso isomer **6b** shows only one. Both **6a** and **6b** have two different types of methylene protons (Figure 3); however, inspection of models shows that those in the racemic compound appear to be in a magnetically less similar environment than those in the meso compound, which may account for the observed spectra.

The stereochemical composition of the allene mixture **5a**, **5b** was shown to be independent of the stereochemistry of the tetrabromide precursor **4**.[1] Thus, either **4a** or **4b** on treatment with methyllithium at $-10°$ gave the same mixture (*ca.* 1:2; nmr) of racemic (**5a**) and meso (**5b**) isomers. This finding is in accord with a stepwise mechanism proceeding through the racemic monoallene **8**, which on further ring expansion



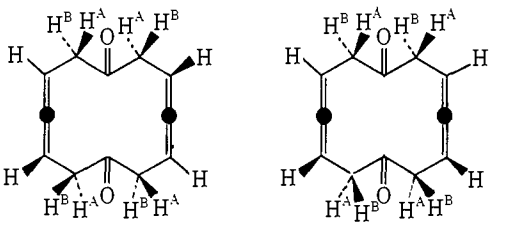
8

gives the mixture of diastereomeric diallenes. Some support for this sequence was obtained by examining the properties of 6,6-dibromo-12,12-dichloro-3,3,8,8-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**11**).

Treatment of **3** with chloroform and potassium *tert*-butoxide gave in 70% yield a mixture (*ca.* 5:1) of 11,-11-dichloro-3,3,8,8-tetramethoxybicyclo[8.1.0]undeca-5-ene (**9**), mp 146–147°, and *anti*-6,6,12,12-tetrachloro-3,3,8,8-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**10**). The stereochemistry assigned to **10** was confirmed by a full X-ray crystallographic analysis.[6] Reaction of **9** with bromoform and potassium *tert*-butoxide gave 80% of 6,6-dibromo-12,12-dichloro-3,3,8,8-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**11**), mp 167–168° (Scheme II). The nmr spectrum of **11** showed singlets at τ 6.71 and 6.73, due to the methoxyl protons, multiplets at 7.90 and 8.38 due to the methylene protons, and a multiplet at 8.77, due to the cyclopropane protons. Compound **11** could also be prepared by the reverse sequence, namely reaction of **3** with bromoform and then chloroform in the presence of potassium *tert*-butoxide. However, **12** was only a minor product of **3** with bromoform,[7] whereas **9** was the major product with chloroform.

Treatment of **11** with methyllithium at $-10°$ gave 60% of the monoallene **13**, mp 90–91°. Only the dibromocyclopropane ring has reacted under the conditions, as expected from previous observations.[2] The ir spectrum (KBr) of **13** showed an absorption at 1960 cm^{-1} attributed to the allene group, and the nmr spectrum had absorptions in the allene (τ 4.95) and cyclopropane (8.54–8.84) regions.

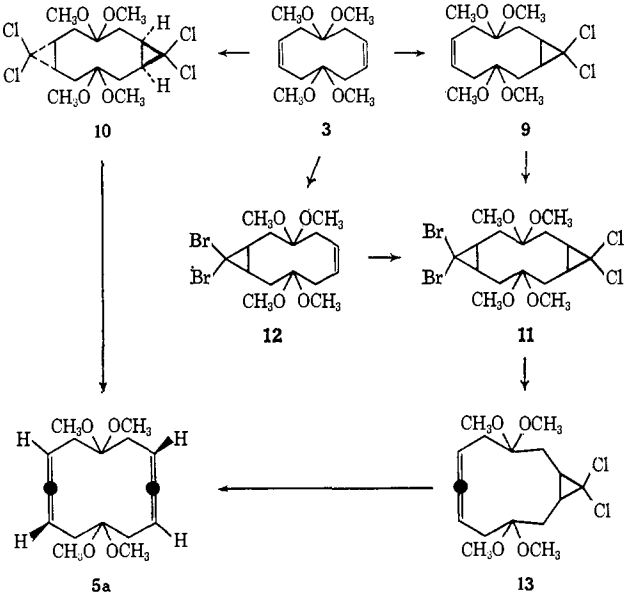
Reaction of **13** with *n*-butyllithium at $-10°$ gave, as sole product, the racemic diallene **5a** in 25% yield. The production of only the racemic diallene under these conditions is presumably due to the destruction



6a **6b**

Figure 3.

Scheme II

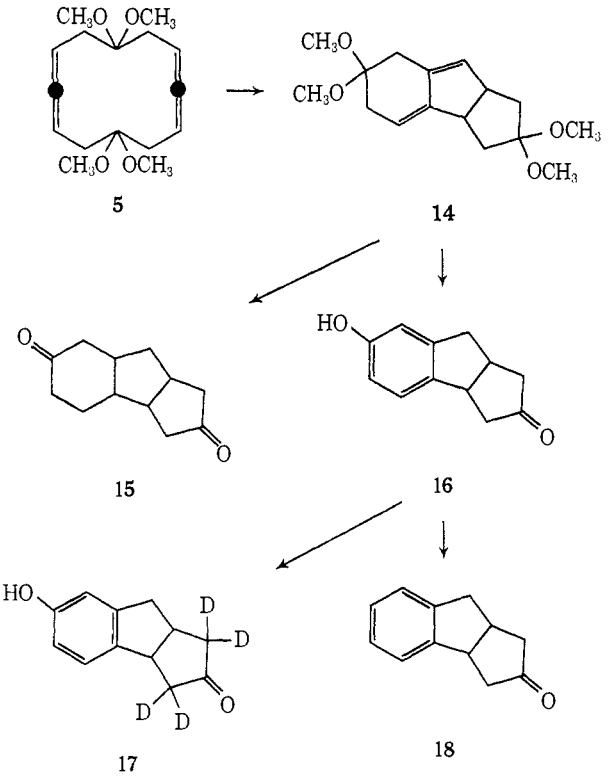


of the meso isomer. Thus, when a mixture of diastereomeric racemic and meso diallenes **5a**, **5b** was treated with *n*-butyllithium at $-10°$, the meso isomer was destroyed, and only the racemic compound remained. The racemic diallene **5a** was also the only product obtained when either the anti tetrabromide **4a** or the anti tetrachloride **10** was treated with *n*-butyllithium. In fact, the simplest preparation of pure racemic **5a** is from one of these reactions with *n*-butyllithium.

Reaction of the tetrabromide **4a** with methyllithium under more vigorous conditions resulted in a new product, presumably derived from the diallenes **5a**, **5b**. This was confirmed by treatment of either the racemic or meso diallenes **5a**, **5b** with methyllithium in refluxing ether, which led to the tricyclic compound **14**, mp 82–83°, in *ca.* 50% yield. The structure assigned to **14** is based on its spectral properties and chemical transformations. Hydrogenation of **14** over palladium on charcoal in EtOAc, with concomitant hydrolysis, gave the saturated dione **15**, mp 55–56°, substantiating the tricyclic nature of **14** (Scheme III). The ir spectrum of **14** (1738, 1718 cm^{-1}) indicated the presence of both a five-and a six-membered ring ketone. Reaction of **14** with dilute acid gave the phenol **16**, mp 127–128°, in 80% yield. The ease of formation of the phenol group indicated the availability of a dienone system in **14**, and the electronic spectrum of **14** [λ_{max}^{EtOH} 244.5 nm (ϵ 17,000)] was suggestive of a heteroannular diene. The ir spectrum of **16** (1735 cm^{-1}) confirmed the presence of a five-membered ring ketone, and the nmr spectrum indicated the position of the hydroxyl group. Treatment of **16** with sodium methoxide in

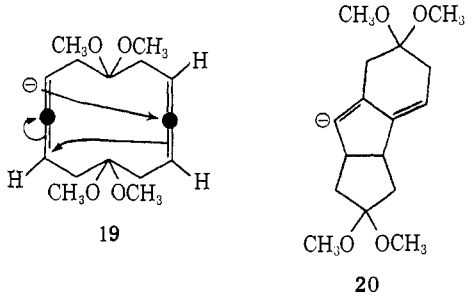
Chem. Soc., **83**, 2013 (1961); R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962); P. J. Garratt and F. Sondheimer, *J. Chem. Soc. C*, 565 (1967).

Scheme III



CH_3OD gave the tetradeuterio derivative **17**, confirming that the ketone had four adjacent methylene protons. Reaction of **16** with 5-chloro-1-phenyltetrazole and subsequent hydrogenation of the product[12] gave the known ketone **18**, mp 33–34°, the spectra of which were identical with those of an authentic sample.[13] This comparison confirms the carbon skeleton of **14**.

The rearrangement of **5** to **14** possibly proceeds *via* the anion **19**, this type of allenic anion having been well authenticated;[14] **19** then undergoes intramolecular cyclization, as shown, to give the anion **20**, followed by protonation.



The diallene mixture **5** is a suitable intermediate for the preparation of a range of monocyclic products containing 12 or more carbon atoms. We have already reported[15] the ring expansion of **5** to the corresponding 14-membered ring dicumulene, and the synthesis of other 12- and 14-membered monocyclic systems will now be described. Reduction of the diastereomeric mixture **5** with sodium in liquid ammonia at −78°[16] gave a crystalline product (85%), from which the pure diene **21**, mp 128–130°, was isolated (36% yield from **5**) by fractional crystallization. The mother liquors contained **21** together with three isomeric diketals. These four compounds could not be separated further, but hydrolysis resulted in the corresponding four diones which were separately isolated (see below).

The structure **21** assigned to the pure diketal was based on spectral and degradative evidence. The nmr spectrum [τ 4.70 (m, 4 H, olefinic), 6.90 (s, 12 H, OCH_3), 7.67 (d, J = 8 Hz, 4 H, H^3, H^9), 7.98 (m 4 H, H^6, H^{12}), 8.60 (m, 4H, H^5, H^{11})] was in accord with structure **21** and confirmed that the molecule was symmetric. The ir spectrum indicated the presence of only cis double bonds (708, 755 cm^{-1}), with no significant absorption peaks in the 960–1000-cm^{-1} region. Ozonolysis of **21** in absolute ethanol, followed by successive reduction with sodium borohydride, acid hydrolysis, and acetylation with acetic anhydride, gave 1,3,6-hexanetriol triacetate (**22**) in 77% yield as the only product. The nmr spectrum [τ 5.10 (m, 1 H, H^3), 6.02 (m, 4 H, H^1, H^6), 8.05, 8.07 (singlets, 9 H, CH_3CO), 8.16–8.68 (m, 6 H, H^2, H^4, H^5)] was in agreement with the assigned structure **22**. Hydrolysis of **21** with *p*-toluenesulfonic acid and boron trifluoride etherate in acetone gave the dione **23**, mp 118–119°.

Reaction of **21** with excess bromoform and potassium *tert*-butoxide gave a mixture of the mono(dibromocarbene) adduct and the bis(dibromo carbene) adduct **24**, from which **24** (mp 129–130° dec) could be separated in 44% yield by fractional crystallization (Scheme IV). Treatment of **24** with methyllithium in ether at −10° gave a mixture of the two diastereomeric diallenes **25a** and **25b**, in 90% yield. The meso diallene **25b** (mp 142–143°) could be obtained pure by fractional cystallization of the mixture. Preparative tlc of the mother liquors gave the pure racemic diallene **25a** (mp 107–108°).

The gross structure of the allenes **25a** and **25b** is based on the mode of formation and the hydrogenation and concomitant hydrolysis of each isomer over platinum to the known cyclotetradecane-1,8-dione (mp 148–149° (lit.[17] 147–148°)). The stereochemical assignments are again based on a partial asymmetric synthesis. Reaction of **24** with methyllithium in the presence of (−)-sparteine[10] gave the diastereomeric diketal mixture; after separation, the isomer, mp 105–107°, showed an optical rotation ($[\alpha]^{20}D$ +12.20 ± 0.05°), whereas the isomer, mp 142–143°, was found to be optically inactive. Thus, the compound, mp 107–108°, is the racemic isomer **25a**, and the compound, mp 142–143°, is the meso isomer **25b**.

The nmr spectrum of the meso isomer **25b** showed two methoxyl signals, which is in agreement with the clear difference in the environment of the two methoxyl groups with respect to the allene protons. The nmr spectrum of the racemic isomer **25a** showed only one methoxyl band in a variety of solvents. Although the methoxyl groups in **25a** are not equivalent, the

(12) W. J. Muslimer and J. W. Gates, *J. Amer. Chem. Soc.*, **88**, 4271 (1966).

(13) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 2957 (1971).

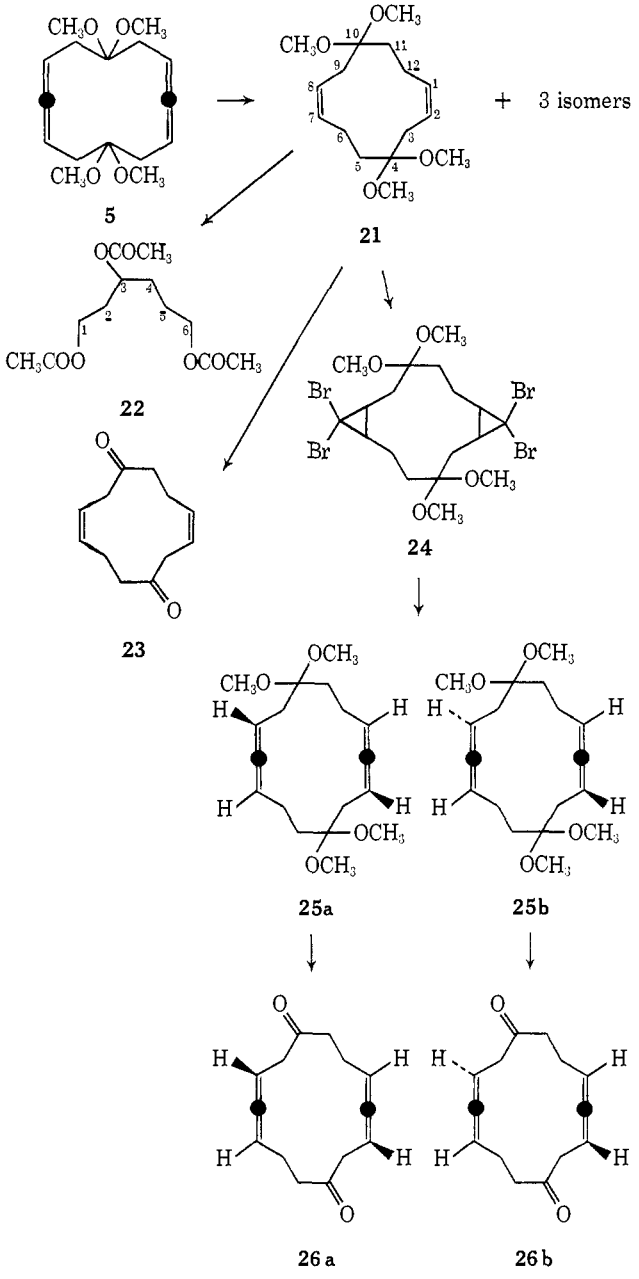
(14) See Y. Leroux and R. Mantione, *Tetrahedron Lett.*, 591 (1971); R. Mantione and Y. Leroux, *ibid.*, 593 (1971).

(15) P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Chem. Commun.*, 1018 (1971).

(16) See D. Devaprabhakara and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 648 (1963); R. Vaidyanathaswamy and D. Devaprabhakara, *J. Org. Chem.*, **32**, 4143 (1967), and references therein.

(17) A. T. Blomquist and R. D. Spencer, *J. Amer. Chem. Soc.*, 70, 30 (1948); F. Sondheimer and Y. Gaoni, *ibid.*, **81**, 6301 (1959).

Scheme IV



difference in the environment is small, depending only on whether one or two methylene groups intervene between the methoxyl group and the allene.

Hydrolysis of **25a** with *p*-toluenesulfonic acid and boron trifluoride etherate in acetone gave the corresponding dione **26a**, mp 114–115°, and similar hydrolysis of **25b** gave **26b**, mp 151–152°. In practice it was found that the preferred method for the preparation of **26a**, **26b** was to hydrolyze the ketal mixture **25a**, **25b** and to separate the isomeric diones (tlc). The gross structure of **25a**, **25b** was supported by the spectral data and was confirmed by the catalytic hydrogenation of each isomer over platinum to cyclotetradecane-1,8-dione. Hydolysis of the ketals **25a** and **25b** prepared by the partial asymmetric synthesis gave optically active **26a**, mp112–113°, $[\alpha]^{20}D$ +34.10 ± 0.05°, and optically inactive **26b**, respectively. The nmr spectra of **26a** and **26b** are shown in Figure 4.

As was previously mentioned, the reduction of **5** with sodium in liquid ammonia gave a mixture of

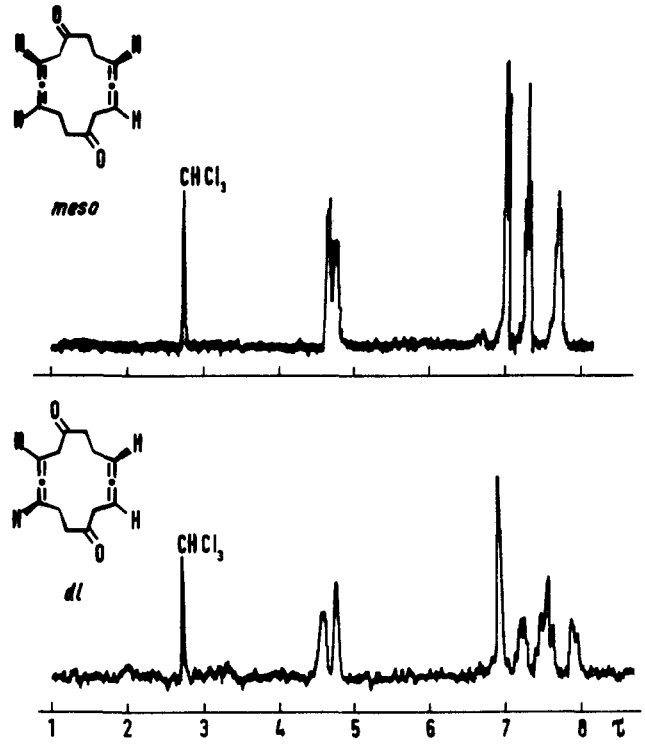
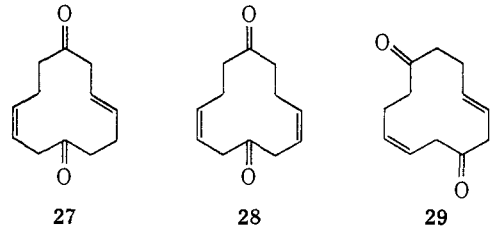


Figure 4. Nmr spectra (220 MHz) of racemic (**26a**) and meso (**26b**) 3,4,10,11-cyclotetradecatetraene-1,8-diones in $CDCl_3$ with TMS as internal standard.

isomeric ketals. Although only the pure ketal **21** could be obtained, hydrolysis of the mother liquors with *p*-toluenesulfonic acid and boron trifluoride etherate in acetone led to a mixture of cyclododecadienediones, from which four isomers could be separated by preparative tlc on silica. Besides the previously described *cis,cis*-3,9-cyclododecadiene-1,7-dione (**23**), mp 118–119° (6%), the other isomers were identified as *cis,trans*-3,9-cyclododecadiene-1,7-dione (**27**), mp 57–58° (12%), *cis,cis*,-3,10-cyclodocecadiene-1,7-dione (**28**), colorless oil (5%), and *cis,trans*-3,10-cy-



clododecadiene-1,7dione (**29**), mp 69–70°. The yields of **27** and **28** were approximately constant from a number of reductions, whereas that of **29** varied from *ca.* 10% to *ca.* 1%.

The position of the double bonds in **27** was established by successive ozonolysis, reduction, and acetylation to give **22**, identical with the sample obtained from **21**. The cis,trans arrangement of the double bonds was assigned on the basis of the ir and nmr spectra. The compound **28** did not give **22** on ozonolysis, suggesting that the double bonds were not symmetrically arranged, and the ir and nmr spectra indicated the presence of only cis double bonds. The compound **29** was assigned the indicated structure on the basis of the ir and nmr spectra. The nmr spectra and the

relevant bands in the ir spectra of **23**, **27**, **28**, and **29** are collected in Table I. The assignment of the protons

Table I. The Ir and Nmr Spectra of the Cyclododecadienediones **23**, **27**, **28**, and **29**

Compd	Nmr spectrum ($CDCl_3$, 100 MHz, τ)	Ir spectrum (KBr,[a] cm^{-1})
23	4.30–4.46 (m, 4 H, H^3, H^4, H^9, H^{10}) 6.82 (d, J = 6 Hz, 4 H, H^2, H^8) 7.56 (bs, 8 H, H^5, H^6, H^{11}, H^{12})	710 (s)
27	4.24–4.74 (m, 4 H, H^3, H^4, H^9, H^{10}) 6.91 (d, J = 6 Hz, 2 H, H^2) 7.01 (d, J = 5 Hz, 2 H, H^8) 7.40–7.76 (m, 8 H, H^5, H^6, H^{11}, H^{12})	708 (s) 985 (s)
28	4.08–4.72 (m, 4 H, H^3, H^4, H^{10}, H^{11}) 6.85 (d, J = 6 Hz, 4 H, H^2, H^{12}) 7.36–7.73 (m, 8 H, H^5, H^6, H^8, H^9)	743 (s)[b]
29	4.22–4.58 (m, 4 H, H^3, H^4, H^{10}, H^{11}) 6.83 (d, J = 6 Hz, 2 H, H^2) 7.01 (d, J = 5 Hz, 2 H, H^{12}) 7.38–7.86 (m, 8 H, H^5, H^6, H^8, H^9)	710 (m) 1000 (m)

[a] (s) = strong, (m) = medium intensity. [b] Liquid film.

in the nmr spectra is based on the chemical shifts and the apparent slightly larger coupling of the isolated methylene protons to the olefinic proton in the cis configuration. Overall, the sodium–liquid ammonia reduction of **5** gives predominately the cis olefin, a finding in accord with previous reports on the reduction of other allenes.[16]

Experimental Section

Nmr spectra were obtained on a Varian HA-100 spectrometer and are recorded in τ units as solutions in $CDCl_3$ with TMS as internal standard, except as stated otherwise. Mass spectra (MS) were taken on an A.E.I. MS-12 or MS-9 spectrometer at 70 eV. Infrared spectra were recorded either on a Unicam SP 200 or a Perkin-Elmer 257 spectrophotometer, only strong and medium bands being reported, and electronic spectra were determined on either a Unicam SP 800 or a Cary 14 recording spectrophotometer. Optical rotations were measured on a Bendix NPL automatic polarimeter Type 143, which was calibrated with standard solutions of (+)-sucrose.

Silica for preparative thin layer chromatography (ptlc) was Merck Kieselgel PF_{254} and alumina for ptlc was Merck PF_{254} (type E). Alumina for column chromatography was Woelm Neutral (Activity II–III), and silica was Hopkins and Williams Silica gel (MFC). Bromoform was dried over $CaCl_2$ and freshly distilled from P_2O_5 under N_2. Methyllithium was in ether and *n*-butyllithium was in *n*-hexane, both from Alfa Inorganics. Solvents were purified and dried by standard methods.

Reaction of 4,4,9,9-Tetramethoxy-1,6-cyclodecadiene (3) with Bromoform and Potassium *tert*-Butoxide. Synthesis of *anti*- (4a) and *syn*- (4b) 6,6,12,12-Tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane. The diketal **3** (12.8 g, 0.05 mol) and potassium *tert*-butoxide (63 g, 0.56 mol) were added to dry pentane (1.5 l.), and the suspension was stirred and cooled to 0° under N_2. Bromoform (94.9 g, 0.37 mol) was added slowly over 4 hr with continued stirring, and the mixture was then allowed to come to room temperature and stirred for a further 12 hr. The insoluble material was then removed by filtration, and the precipitate was successively washed with water (4 × 500 ml), methanol (2 × 200 ml), chloroform (100 ml), and ether (2 × 100 ml) and dried under vacuum, when *anti*-6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0.^{5,7}]dodecane (**4a**) (24 g, 80%) was obtained as an amorphous powder (mp 180–182° dec). Slow recrystallization (CH_2Cl_2) of a portion of the material gave crystalline **4a** (mp 155–156°), spectroscopically identical (ir, nmr) with the amorphous material: ms *m/e* 541, 539, 537 (3.5%), 535, 533 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 523, 521, 519 (2.5%), 517 (1:3:3:1, M^+ − Br), 491, 489, 487 (6%), 485 (1:3:3:1, $M^+ - CH_4OBr$), 459, 457, 455 (3%), 453 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 345, 343 (8%), 341 (1:2:1, $M^+ - C_3H_{13}O_3Br_2$), 303, 301, 299, 221, 219, 105 (100%); ir (KBr) 2950, 1310, 1300, 1288, 1205, 1145, 1110, 1055, 1040, 1004, 990, 834, 770, and 754 cm^{-1}; nmr (CD_2Cl_2) 6.74 (s, 12 H, OCH_3), 7.80–8.20 (m, 8 H, CH_2), 8.70–9.00 (m, 4 H, cyclopropane).

Anal. Calcd for $C_{16}H_{24}O_4Br_4$: C, 32.03; H, 4.03; Br, 53.28. Found: C, 31.90; H, 4.19; Br, 53.16.

The filtrate obtained after removal of the precipitated **4a** was evaporated to small volume and the oily residue chromatographed on silica. Elution with pentane–ether gave *syn*-6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**4b**) (0.52 g, 0.9%): mp 148–149°; ms *m/e* 541, 539, 537 (17%), 535, 533 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 540, 538, 536 (15%), 534, 532 (1:4:6:4:1, $M^+ - C_2H_8O_2$), 523, 521, 519 (14%), 517 (1:3:3:1, M^+ − Br), 491, 489, 487, (12%), 485 (1:3:3:1, $M^+ - CH_4OBr$), 459, 457, 455 (10%), 453 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 303, 301, 299, 275, 273, 271, 221, 219, 105 (100%); ir (KBr) 2960, 2830, 1468, 1458, 1330, 1294, 1273, 1150, 1120, 1052, 1002, 951, 800, 771, 753, and 710 cm^{-1}; nmr 6.70 (s, 6 H, OCH_3), 6.74 (s, 6 H, OCH_3), 7.75 (d, J = 14 Hz, 4 H, CH_2), 8.12 (m, 4 H, CH_2), 8.90 (m, 4 H, cyclopropane).

Anal. Calcd for $C_{16}H_{24}O_4Br_4$: C, 32.03; H, 4.03; Br, 53.28. Found: C, 31.84; H, 3.94; Br, 53.21.

Reaction of 4a and 4b with Methyllithium. Synthesis of Racemic (5a) and Meso (5b) 5,5,11,11-Tetramethoxy-1,2,7,8-cyclododecatetraene. The anti isomer **4a** (6 g, 10 mmol) was suspended in dry ether (50 ml), and the mixture was stirred and cooled to −80° under N_2. Methyllithium (20 ml, 1.5 *M*, 30 mmol) was added in one portion, and the reaction mixture was then allowed to warm to −10° and stirred at this temperature for 1 hr, during which time all of **4a** dissolved. Water (25 ml) was added, and the etheral layer was separated. The aqueous layer was extracted with ether (50 ml), and the combined ethereal layers were extracted with water (2 × 10 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a residue which on crystallization gave colorless crystals (2.2 g). Ptlc (silica) with pentane–ether (85:15) gave, after recrystallization (pentane), the following.

(i) ***rac*-5,5,11,11-Tetramethoxy-1,2,7,8-cyclododecatetraene (5a)**: mp 116–117.5°; ms *m/e* 280 (M^+, 12.5%), 265 ($M^+ - CH_3$), 249 ($M^+ - CH_3O$), 248 ($M^+ - CH_4O$), 233, 217, 216, 201, 185, 88 (100%); ir (KBr) 2950, 2825, 1970, 1460, 1440, 1300, 1275, 1218, 1197, 1115, 1065, 1053, 967, 881, 865, 859, and 766 cm^{-1}; nmr 4.90–5.14 (m, 4 H, allene), 6.80 (s, 12 H, OCH_3), 7.34–7.98 (m, 8 H, CH_2).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.56; H, 8.94.

(ii) ***meso*-5,5,11,11-Tetramethoxy-1,2,7,8-cyclododecatetraene (5b)**: mp 86–87.5°; ms *m/e* 280 (M^+, 4%), 265 ($M^+ - CH_3$) 249 ($M^+ - CH_3O$), 248 ($M^+ - CH_4O$), 233, 217, 216, 185, 160, 125, 121, 105, 101, 89, 88 (100%); ir (KBr) 2950, 2830, 1970, 1465, 1458, 1440, 1303, 1278, 1225, 1194. 1114, 1074, 1055, 1040, 1010, 929, 888, 867, 854, 805, 784, and 724 cm^{-1}; nmr 4.98–5.24 (m, 4 H, allene), 6.80 (s, 12 H, OCH_3), 7.52–7.70 (m, 8 H, CH_2)

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.44; H, 8.93.

The syn isomer **4b** (600 mg, 1 mmol) was reacted with methyllithium under the same conditions as the anti isomer, and the same (nmr, ir) crystalline mixture (230 mg, 82%) of racemic and meso isomers was obtained. The mixture of diastereomers was separated as described and the racemic and meso isomers were identified with those obtained from the anti isomer (ir, nmr, mixture melting point).

***rac*-3,4,9,10-Cyclododecatetraene-1,7-dione (6a).** The diketal **5a** (100 mg, 0.3 mmol) was dissolved in ether (10 ml), and sulfuric acid (5%, 2.5 ml) was added and the mixture was shaken for 10 hr. The ethereal layer was separated, the aqueous layer was extracted with ether (2 × 10 ml), and the combined ethereal extracts were dried ($MgSO_4$). Evaporation of the solvent and crystallization (pentane) gave *rac*-cyclododeca-3,4,9,10-tetraene-1,7-dione (**6a**) (50 mg, 75%) as colorless plates: mp 96–97°; ms *m/e* 188 (M^+, 1%), 160 ($M^+ - H_2O$), 145, 132, 131, 117, 91, 66, 65, 51, 39 (100%); ir (KBr) 2960, 2910, 1960, 1710, 1440, 1412, 1350, 1320, 1253, 1219, 1180, 1097, 988, 890, and 737 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 227 nm sh (ε 1300), 295 (240).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.48; H, 6.72.

***meso*-3,4,9,10-Cyclododecatetraene-1,7-dione (6b).** The diketal **5b** (100 mg, 0.3 mmol) was hydrolyzed by the same method as for **5a**, giving *meso*-cyclododeca-3,4,9,10-tetraene-1,7-dione (**6b**) (50 mg, 75%) as colorless plates: mp 67–68°; ms *m/e* 118 (M^+, 26%), 160 ($M^+ - H_2O$, 29%), 145, 132, 131, 117 (97%), 91, 66, 65, 51, 40 (100%), 39 (100%); ir (KBr) 2950, 1960, 1710, 1410, 1344, 1250, 1224, 1175, 1164, 1160, 1100, 1020, 900, 867, 845, and

710 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 230 nm sh (ϵ 1380), 296 (340).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.39; H, 6.56.

Catalytic Hydrogenation of Racemic (6a) and Meso (6b) 3,4,9,10-Cyclododecatetraene-1,7-diones. The dione **6a** (18.8 mg, 0.1 mmol) was dissolved in ethyl acetate (5 ml) containing prereduced platinum dioxide (20 mg), and the mixture was stirred under hydrogen for 1 hr. Removal of the catalyst and evaporation of the solvent gave, after crystallization from pentane, cyclododeca-1,7-dione (**7**) (16 mg, 81%) as colorless needles: mp 134–135° (lit.[9] 134–136°); ms *m/e* 196 (M^+, 20%), 178 ($M^+ - H_2O$, 26%), 149, 111, 98, 97, 96, 95, 83, 81, 71, 70, 69, 67, 55 (100%), 41; ir (KBr) 2950, 2860, 1700, 1478, 1440, 1430, 1377, 1255, 1178, 1160, 1125, 1036, 1025, 990, 808, 741, and 733 cm^{-1}; nmr 7.50–7.70 (m, 6 H), 7.85 (s, 4 H), 8.07–8.48 (m, 6 H), 8.67–8.96 (m, 4 H). Compound **7** was also obtained when **6b** was hydrogenated under the same conditions.

Partial Asymmetric Synthesis of the Racemic Diallenes 5a, 6a. The antiisomer (**4a**) (3 g, 5 mmol) was suspended in dry ether (100 ml) and (−)-sparteine (7.02 g, 30 mmol) was added. The mixture was cooled (−80°) and stirred under N_2, and methyllithium (30 ml, 1 *M*, 30 mmol) was added in one portion. The reaction mixture was allowed to warm to −10° and stirred for a further 1 hr, and water (25 ml) was added. The ethereal layer was separated, and the aqueous phase was extracted with ether (25 ml). The combined ethereal layers were washed with sulfuric acid (5%, 2 × 50 ml) and saturated NaHCO and dried ($MgSO_4$). Filtration through alumina and evaporation of the solvent gave a mixture of diastereomers, which were separated by ptlc on silica to give **5a** and **5b**. The compound **5a**, mp 114–116°, was optically active, $[\alpha]^{20}D$ +24.45 ± 0.05° (*c* 2.3 g/100 ml, *n*-hexane). The compound **5b** was optically inactive. Acid hydrolysis of the diketal **5a** as described previously gave the dione **6a**, mp 94–96°, which was optically active, $[\alpha]^{20}D$ +55.55 ± 0.05° (*c* 0.88 g/100 ml, ethanol). Similar hydrolysis of **5b** gave the optically inactive **6b**.

Synthesis of 11,11-Dichloro-3,3,8,8-tetramethoxybicyclo[8.1.0]-undec-5-ene (9) and *anti*-6,6,12,12-Tetrachloro-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (10). The diketal (**3**) (256 mg, 1 mmol) was dissolved in a mixture of pentane (5 ml) and chloroform (5 ml), and the mixture was stirred and cooled to 0° under N_2. Potassium *tert*-butoxide (4.48 g, 40 mmol) was added in portions over 2 hr; the reaction mixture was then allowed to come to room temperature and was stirred for a further 30 min. Water (30 ml) was added and the mixture extracted with CH_2Cl_2 (100 ml). The organic phase was washed with water (20 ml), dried ($MgSO_3$), and concentrated to small volume. Ptlc on silica, eluting with CH_2Cl_2, gave the following.

(i) ***anti*-6,6,12,12-Tetrachloro-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (10)** (30 mg, 7%), colorless crystals (CH_2Cl_2): mp 161–163°; ms *m/e* 428 426 (0.1%), 424, 422, 420 (1:12:56:113:87, M^+), 391, 389, 387 (10%), 385 (1:10:30:30, $M^+ - Cl$), 361, 359, 357, 355, 353, 211, 177, 175, 129, 105 (100%), 89, 88, 75; ir (KBr) 2950, 2825, 1455, 1308, 1287, 1204, 1144, 1105, 1054, 1038, 1008, 994, and 822 cm^{-1}; nmr 6.77 (s, 12 H, OCH_3), 7.80–8.05 (m, 4 H, CH_2), 8.38–8.55 (m, 4 H, CH_2), 8.63–8.92 (m, 4 H, cyclopropane).

Anal. Calcd for $C_{16}H_{24}O_4Cl_4$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.42; H, 5.77; Cl, 33.58.

(ii) **11,11-Dichloro-3,3,8,8-tetramethoxybicyclo[8.1.0]undec-5-ene (9)** (103 mg, 30%), colorless crystals (pentane): mp 146–147°; ms *m/e* 342, 340, 338 (4.5%), (1:6:9, M^+), 310, 308, 306 (17%), (1:6:9, $M^+ - CH_4O$), 279, 277, 275, (32%) (1:6:9, $M^+ - C_2H_7O_2$), 273, 271, (21%) (1:3, $M^+ - CH_4OCl$), 192, 161, 153, 109 (100%), 108, 105, 75; ir (KBr) 2970, 2840, 1465, 1453, 1312, 1282, 1267, 1223, 1195, 1139, 1128, 1064, 1055, 1043, 1015, 980, 950, 836, 829, 790, and 717 cm^{-1}; nmr 4.52–4.67 (m, 2 H, olefin), 6.77, 6.79 (s, 12 H, OCH_3), 7.40–7.44 (m, 4 H, CH_2), 7.95 (dd, J = 2.5, 15 Hz, 2 H, CH_2), 8.35 (dd, J = 2.5, 6.5 Hz, 2 H, CH_2), 8.84 (ddd, J = 2.5, 6.5, 15 Hz, 2 H, cyclopropane).

Anal. Calcd for $C_{15}H_{24}O_4Cl_2$: C, 52.94; H, 7.06; Cl, 20.88. Found: C, 53.26; H, 7.26; Cl, 21.18.

The starting diketal **3** (128 mg, 50%) was also recovered.

Synthesis of 6,6-Dibromo-12,12-dichloro-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (11). The dichloride **9** (85 mg, 0.25 mmol) and potassium *tert*-butoxide (280 mg, 2.5 mmol) were added to pentane (20 ml), and the mixture was stirred and cooled to 0° under N_2. Bromoform (630 mg, 2.5 mmol) in pentane (2 ml) was slowly added, and the reaction mixture was then allowed to come to room temperature and stirred for a further 30 min. Water (10 ml) was added, the mixture was extracted with CH_2Cl_2 (50 ml), and the organic phase was washed with water (5 ml) and dried ($MgSO_4$). Removal of the solvent gave 6,6-dibromo-12,12-dichloro-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**11**) (100 mg, 80%): mp 167–168° (pentane); ms *m/e* 516, 514, 512, 510 (0.2%), 508 (1:8:23:26:10, M^+), 479, 477, 475 (5%), 473 (1:5:7:3, $M^+ - Cl$), 451, 449, 447, 445, 443, 441, 435, 433, 431 (12%), 429 (1:7:16:10, $M^+ - Br$), 403, 401, 399 (12%), 397 (1:7:16:10, $M^+ - CH_4OBr$), 370, 368, 366, 364, 362, 360, 358, 356, 354, 221, 219, 211, 175, 105 (100%); ir (KBr) 2950, 1453, 1305, 1288, 1205, 1147, 1108, 1055, 1040, 1004, 991, 833, 798, and 768 cm^{-1}; nmr 6.71, 6.73, (s, 12 H, OCH_3), 7.76–8.03 (m, 4 H, CH_2), 8.23–8.55 (m, 4 H, CH_2), 8.61–8.92 (m, 4 H, cyclopropane).

Anal. Calcd for $C_{16}H_{24}O_4Br_2Cl_2$: C, 37.60; H, 4.73; Br, 31.27; Cl, 13.87. Found: C, 37.29; H, 4.58; Br, 31.40; Cl, 13.90.

The compound **11** (164 mg, 63%) could also be prepared by reaction of the dibromide **12** (224 mg, 5 mmol) and potassium *tert*-butoxide (1.12 g, 10 mmol) in pentane (30 ml) with $CHCl_3$ (1.2 g, 10 mmol) in pentane (4 ml) at 0° under N_2.

Synthesis of 12,12-Dichloro-3,3,9,9-tetramethoxybicyclo[9.1.0]-dodeca-5,6-diene (13). The compound **11** (102 mg, 0.2 mol) was suspended in ether (10 ml), and the mixture was stirred and cooled to −80° under N_2. Methyllithium (0.4 ml, 1 *M*, 0.4 mmol) was added in one portion and the reaction mixture was allowed to warm to −10° and stirred for a further 30 min. Water (2 ml) was added, the ethereal layer was separated, and the aqueous phase was washed with ether (10 ml). The combined organic layers were washed with water (2 ml) and dried ($MgSO_4$). Evaporation of the solvent gave an oily residue, which, after ptlc on silica, eluting with pentane–ether (20:80), gave 12,12-dichloro-3,3,9,9-tetramethoxybicyclo[9.1.0]dodeca-5,6-diene (**13**) (44 mg, 60%) as colorless crystals (pentane): mp 90–91°; ms *m/e* 354, 352, 350 (2%), (1:6:9, M^+), 339, 337, 335 (2.5%) (1:6:9, $M^+ - CH_3$), 317, 315 (12%) (1:3, $M^+ - Cl$), 291, 289, 287 (35%) (1:6:9, $M^+ - C_2H_7O$), 285, 283 (22%) (1:3, $M^+ - CH_4OCl$), 253, 251, 247, 232, 195, 185, 183, 141, 140, 109, 105, 89, 88 (100%); ir (KBr) 2940, 2820, 1960, 1455, 1441, 1305, 1285, 1273, 1246, 1236, 1152, 1120, 1108, 1063, 1040, 988, 974, 895, 886, 883, 825, 805, and 719 cm^{-1}; nmr 4.95 (m, 2 H, allene), 6.76 (s, 3 H, OCH_3), 6.78 (s, 3 H, OCH_3), 6.80 (s, 6 H, OCH_3), 7.24–8.54 (m, 8 H, CH_2), 8.54–8.84 (m, 2 H, cyclopropane).

Anal. Calcd for $C_{16}H_{24}O_4Cl_2$: C, 54.71; H, 6.89. Found: C, 54.45; H, 6.68.

Reaction of 12,12-Dichloro-3,3,9,9-tetramethoxybicyclo[9.1.0]-dodeca-5,6-diene (13) with *n*-Butyllithium. The compound **13** (70.2 mg, 0.2 mmol) was dissolved in ether (10 ml), and the solution was stirred and cooled to −80° under N_2. *n*-Butyllithium (0.2 ml, 2 *M*, 0.4 mmol) was added in one portion and the reaction mixture was allowed to warm to −10° and was then stirred for a further 30 min. Water (2 ml) was added, the organic layer was separated, and the aqueous phase was extracted with ether (10 ml). The combined organic layers were washed with water (2 ml) and dried ($MgSO_4$). Evaporation of the solvent gave an oily mixture containing at least six compounds (tlc), which on ptlc on silica, eluting with pentane–ether (85:15), gave the racemic allene **5a** (16 mg, 28%), identical in all observed respects with an authentic sample. No meso isomer **5b** was observed.

The allene **5a** was also obtained, again in the absence of the meso isomer **5b**, when the anti tetrabromide **4a**, the anti tetrachloride **10**, or compound **11** were treated with *n*-butyllithium under the same conditions.

Reaction of the Mixture of Racemic (5a) and Meso (5b) 5,5,11,11-Tetramethoxy-1,2,7,8-cyclododecatetraenes with *n*-Butyllithium. A mixture (280 mg, 1 mmol) of the diastereomeric diallenes **5a, 5b** was dissolved in ether (20 ml), and the solution was stirred and cooled to −80° under N_2. Addition of *n*-butyllithium (1 ml, 2 *M*, 2 mmol) and subsequent reaction and work-up as described for compound **13** led to racemic **5a** (82 mg) and the complete destruction of **5b**.

Reaction of the Mixture of Racemic (5a) and Meso (5b) 5,5,11,11-Tetramethoxy-1,2,7,8-cyclododecatetraenes with Methyllithium in Boiling Ether. A mixture (1.40 g, 5 mmol) of the diastereomeric diallenes **5a, 5b** was dissolved in ether (25 ml), and methyllithium (5 ml, 1 *M*, 5 mmol) was added in one portion under N_2. The reaction mixture was then heated under reflux for 4 hr, cooled, and quenched with water (5 ml). The organic layer was separated, washed with water (5 ml), and dried ($MgSO_4$). Evaporation of the solvent gave an oil, which on ptlc on silica, eluting with pentane–ether (85:11), gave (i) the unreacted racemic diallene **5a** (200 mg, 14%) and (ii) 5,5,11,11-tetramethoxytricyclo[7.3.0.0^{3,8}]dodeca-2,7-diene (**14**) (550 mg, 40%): mp 82–83° (pentane); ms *m/e* 280

(M^+, 20%), 249 ($M^+ - OCH_3$, 30%), 248 ($M^+ - CH_4O$, 100%) 233 ($M^+ - C_2H_7O$, 63%), 207 ($M^+ - C_2H_7O_2$, 47%) 201, 185, 59; ir (KBr) 2940, 2900, 2825, 1475, 1450, 1355, 1328, 1263, 1245, 1230, 1223, 1183, 1174, 1130, 1103, 1081, 1055, 1045, 1035, 1016, 993, 913, 894, 813, and 785 cm^{-1}; nmr (220 MHz) 4.40 (d, J = 1 Hz, 1 H, olefin), 4.76 (m, 1 H, olefin), 6.79, 6.82 (s, 12 H, OCH_3), 6.86 (s, 2 H, CH_2), 7.30–8.50 (m, 8 H); λ_{max}^{EtOH} 244.5 nm (ϵ 17,000).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.65; H, 8.22.

Catalytic Hydrogenation of 5,5,11,11-Tetramethoxytricyclo[7.3.0.0^{3,8}]dodeca-2,7-diene (14). The compound **14** (100 mg, 0.35 mmol) was dissolved in ethyl acetate, palladium (10%) on charcoal was added, and the mixture was stirred under a hydrogen atmosphere for 1 hr. The catalyst was removed by filtration, the filtrate was evaporated, and the oily residue was crystallized (ether–pentane) to give tricyclo[7.3.0.0^{3,8}]dodeca-5,11-dione (**15**) (35 mg, 51%) as colorless plates: mp 55–56°; ms *m/e* 192 (M^+, 95%), 174 ($M^+ - H_2O$, 38%), 164 ($M^+ - CO$, 35%), 149, 135, 134, 123, 122, 121, 109, 108, 107, 97, 96 (100%), 95, 82, 81, 79, 67, 55, 41; ir (CCl_4) 2940, 1738, 1718, 1475, 1415, 1242, 1177, 1160, and 1120 cm^{-1}; nmr 7.0–9.0 (m).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.73; H, 8.27.

Acid Hydrolysis of 14. The compound **14** (140 mg, 0.5 mmol) was dissolved in ether (25 ml), sulfuric acid (80%, 2.5 ml) was added, and the mixture was shaken at room temperature for 5 min. The organic layer was separated, washed with water (3 × 2 ml), and dried ($MgSO_4$). Evaporation of the solvent gave 6,7-(4-hydroxybenzo)bicyclo[3.3.0]octan-3-one (**16**) (75 mg, 75%): mp 127–128° (pentane–ether); ms *m/e* 188 (M^+, 37%), 159, 146, 145, 131, 105, 86, 84 (100%), 81, 69, 57, 55, 47, 43, 41; ir ($CHCl_3$) 3590, 2930, 2895, 1738, 1610, 1595, 1490, 1445, 1400, 1330, 1260, 1162, 1136, 1085, 860, and 848 cm^{-1}; nmr (220 MHz) 2.87 (d, J = 8.5 Hz, 1 H, benzene, H^6), 3.13 (d, J = 2.5 Hz, 1 H, benzene, H^3), 3.18 (dd, J = 2.5, 8.5 Hz, 1 H, benzene, H^5), 3.70 (s, 1 H, OH), 6.12 (m, 1 H), 6.66–6.82 (m, 2 H, H^8), 7.14–7.47 (m, 4 H), 7.98 (dd, J = 20, 8 Hz); λ_{max}^{EtOH} 216 nm (ϵ 5600), 225 sh (4600), 282 (3000), 287 sh (2700).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; Found: C, 76.45; H, 6.32.

Reaction of 16 with Sodium Methoxide and Methanol-*O*-*d*. The phenol **16** (28.2 mg, 0.15 mmol) was dissolved in CH_3OD (2 ml), and the solution was added to sodium methoxide in CH_3OD (23 mg of sodium in 5 ml of CH_3OD) and stirred under N_2 for 20 hr. The solution was then quenched with D_2O containing a few drops of concentrated HCl until it just became acidic. The solvents were removed by evaporation, and the residue was extracted with ether (25 ml). The ethereal extract was washed with D_2O (2 ml) and dried ($MgSO_4$) and the solvent was evaporated to give the deuterated phenol **17** (20 mg, 70%): mp 127–128°; ms *m/e* 192 (M^+, 4D, 29%), 191 (M^+, 3D, 15%), 148, 147, 146, 131, 111, 109, 97, 95, 83, 81, 71, 69, 67, 57, 55 (100%), 43, 41; ir ($CHCl_3$) 3590, 2950, 2860, 1738, 1612, 1596, 1503, 1460, 1180, and 1140 cm^{-1}; nmr 3.06 (d, J = 8 Hz, 1 H, benzene, H^6), 3.29–3.45 (m, 2 H, benzene, H^3, H^5), 4.10 (s, 1 H, OH), 6.13–6.34 (m, 1 H, H^5), 6.70–7.03 (m, 2 H, H^8), 7.18-7.60 (m, 1.3 H).

Conversion of the Phenol 16 to 6,7-Benzobicyclo[3.3.0]octan-3-one (18). The phenol **16** (188 mg, 1 mmol) was heated to reflux in ethyl methyl ketone (50 ml) with 5-chloro-1-phenyltetrazole (361 mg, 2 mmol) and potassium carbonate (5.50 mg, 4 mmol) for 38 hr. The solvent was removed and the residue extracted with chloroform (50 ml), and the chloroform extract was dried ($MgSO_4$). Evaporation of the solvent, and ptlc on silica, eluting with CH_2Cl_2, gave the tetrazole derivative (210 mg, 63%), mp 144–145° (CH_3OH). The derivative (100 mg, 0.3 mmol) was dissolved in THF (20 ml), palladium on charcoal (10%, 25 mg) was added, and the mixture was stirred under an atmosphere of hydrogen for 48 hr. Removal of the catalyst by filtration and evaporation of the solvent, gave, after ptlc on silica, eluting with pentane–ether (80:20), 6,7-benzobicyclo[3.3.0]octan-3-one (**18**) (30 mg, 55%), mp 33–34° (pentane) (lit.[13] 33–34°); all the observed spectra were identical with those of an authentic sample.[13]

Reduction of the Mixture of Racemic and Meso 5,5,12,12-Tetramethoxy-1,2,7,8-cyclododecatetraenes (5a, 5b). Sodium (2.30 g, 100 mmol) was dissolved in liquid NH_3 (50 ml), the solution was stirred and cooled to −80°, and a solution of the mixture (2.80 g, 10 mmol) of diallene **5a**, **5b** in ether (20 ml) was then added dropwise over 30 min. The reaction mixture was allowed to warm and was stirred at its boiling point for 1 hr, and ammonium chloride was then added until the solution was colorless. The solution was allowed to stand until the NH_3 was lost by evaporation, water (50 ml) was added, and the mixture was extracted with ether (100 ml). The ethereal solution was washed with water (3 × 10 ml) and dried ($MgSO_4$), and the solvent was removed by evaporation to give a crystalline solid (2.40 g). Fractional crystallization of the solid from pentane gave *cis,cis*-4,4,10.10-tetramethoxy-1,7-cyclodecadiene (**21**) (1.0 g, 36%): mp 128–130°; ms *m/e* 284 (M^+, 3%), 252 ($M^+ - CH_3OH$, 3%), 237 ($M^+ - C_2H_7O$, 2%), 221 ($M^+ - C_2H_7O_2$, 2%), 189 ($M^+ - C_3H_{11}O_3$, 9%), 183, 157, 127, 111, 110, 105, 88 (100%), 43; ir (KBr) 2950, 2830, 1470, 1363, 1319, 1293, 1152, 1100, 1063, 1047, 1026, 970, 925, 877, 808, 793, and 733 cm^{-1}; nmr 4.41–5.00 (m, 4 H, olefin), 6.90 (s, 12 H, OCH_3), 7.67 (d, J = 8 Hz, 4 H, CH_2), 7.78–8.14 (m, 4 H, CH_2), 8.43–8.76 (m, 4 H, CH_2).

Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.93. Found: C, 67.54; H, 9.65.

The combined filtrates contained **21** together with three other isomers. These could not be separated, and the mixture was hydrolyzed as described below. Reduction of pure **5a** or **5b** under the same conditions gave the same mixture of products.

Ozonolysis of the Diene 21. The diene **21** (142 mg, 0.5 mmol) was dissolved in absolute ethanol (25 ml) and ozone (3%, 1 l. min^{-1}) was bubbled through the solution for 45 min. The solution was then flushed with O_2 (5 min), sodium borohydride (1 g) was added in one portion, and the solution was heated under reflux for 15 min. After the mixture was cooled, hydrochloric acid (3 *N*) was slowly added to the solution until all gas evolution ceased and the inorganic salts had dissolved. The solvents were removed by evaporation and acetic anhydride (15 ml) was added, and the mixture was then heated under reflux for 15 min. The solvent was removed by evaporation, the residue was extracted with ether (50 ml), and the ethereal solution was dried ($MgSO_4$). Evaporation of the solvent and ptlc of the residue on silica, eluting with pentane–ether, gave hexane-1,3,6-triol triacetate (**22**) (200 mg, 77%) as a colorless oil:[18] ms *m/e* 217 ($M^+ - CH_3O$), 200 ($M^+ - C_2H_4O_2$, 2%), 172, 159, 157, 117, 99, 98, 97, 81, 80, 71, 43 (100%). At higher ion chamber pressure a peak at *m/e* 261 (M + 1) could also be obtained, characteristic of acetates;[19] ir (CCl_4) 2975, 1740, 1460, 1445, 1395, 1375, 1248, 1055, and 1035 cm^{-1}; nmr (CCl_4) 5.00–5.28 (m, 1 H, H^3), 5.91–6.11 (m, 4 H, H^1, H^6), 8.03, 8.05 (s, 9 H, $COCH_3$), 8.32–8.49 (m, 6 H, H^2, H^4, H^5).

Hydrolysis of Compound 21. Compound **21** (142 mg, 0.5 mmol) was dissolved in acetone (5 ml) and *p*-toluenesulfonic acid (5 mg), water (5 drops) and boron trifluoride etherate (1 drop) were added, and the mixture was shaken for 10 min. The solvent was removed by evaporation to give a solid, which was extracted with ether (30 ml). The ethereal solution was washed with water (1 ml) and dried ($MgSO_4$), and the solvent was removed by evaporation. Crystallization (pentane–ether) gave *cis,cis*-3,9-cyclodecadiene-1,7-dione (**23**) (75 mg, 78%): mp 118–119°; ms *m/e* 192 (M^+, 11%), 174 ($M^+ - H_2O$, 5%), 164 ($M^+ - CO$, 2%), 138, 110, 97, 96 (100%), 95, 81, 68, 67, 55, 54, 53, 41, 39; ir (KBr) 3010, 2910, 1700, 1660, 1460, 1440, 1420, 1400, 1348, 1302, 1220, 1178, 1160, 1133, 1068, 1029, 1015 and 710 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 210 nm (ϵ 1550), 291 (135).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.89; H, 8.52.

Reaction of *cis,cis*-4,4,10,10-Tetramethoxy-1,7-cyclodecadiene (12) with Bromoform and Potassium *tert*-Butoxide. Synthesis of 7,7,14,14-Tetrabromo-3,3,10,10-tetramethoxytricyclo[11.1.0.0^{6,8}]tetradecane (24). Compound **12** (284 mg, 1 mmol) was dissolved in pentane (75 ml), bromoform (2.53 g, 10 mmol) was added, and the solution was stirred and cooled to 0° under N_2. Potassium *tert*-butoxide (1.12 g, 10 mmol) was added in portions over 30 min, and the reaction mixture was then allowed to warm to room temperature and was stirred for a further 2 hr. Ether (200 ml) was then added, the mixture was filtered, and the residue was washed with ether (100 ml). The solvent from the combined filtrate and washings was removed by evaporation and the residue crystallized (pentane–ether) to give 7,7,14,14-tetrabromo-3,3,10,10-tetramethoxytricyclo[11.1.0.0^{6,8}]tetradecane (**24**) (280 mg, 44%): mp 129–130° dec; ms *m/e* 568, 566, 564 (26%), 562, 560 (1:4:6:4:1, $M^+ - C_2H_8O_2$), 550, 548, 546 (53%) 544 (1:3:3:1, $M^+ - HBr$), 536, 534, 532 (7%), 530, 528 (1:4:6:4:1, $M^+ - C_3H_{12}O_3$), 518, 516, 514 (10%), 512 (1:3:3:1, $M^+ - CH_3OBr$), 488, 486, 484 (12%), 482, 480 (1:4:6:4:1), 308, 235, 233, 149, 105 (100%), 97; ir (KBr) 2960, 2850, 1467, 1360, 1315, 1285, 1223, 1193, 1160, 1135, 1120,

(18) T. Francis and E. von Rudloff, *Can. J. Chem.*, 37, 972 (1959).

(19) See J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier, Amsterdam, 1968, p 209.

1098, 1069, 1048, 980, 943, 884, 869, 815, 798, 743, and 723 cm^{-1}; nmr 6.74 (s, 6 H, OCH_3), 6.76 (s, 6 H, OCH_3), 7.75–8.50 (m, 12 H, CH_2), 8.54–9.22 (m, 4 H, cyclopropane).

Anal. Calcd for $C_{18}H_{28}O_4Br_4$: C, 34.42; H, 4.49; Br, 50.90. Found: C, 34.46; H, 4.51; Br, 51.17.

A second crop of crystals (160 mg) was contaminated with the mono(dibromocarbene) adduct.

Reaction of 24 with Methyllithium. Preparation of Racemic (25a) and Meso (25b) 5,5,12,12-Tetramethoxy-1,2,8,9-cyclotetradecatetraenes. Compound **24** (314 mg, 0.5 mmol) was suspended in ether (20 ml); the mixture was stirred and cooled to −80° under N_2. Methyllithium (1.5 ml, 1 *M*, 1.5 mmol) was added in one portion; the reaction mixture was allowed to warm to −10° and stirred for a further 30 min. Water (2 ml) was added; the ethereal layer was separated, washed with water (2 ml), and dried ($MgSO_4$). Evaporation of the solvent gave a crystalline mixture (140 mg, 91%) of the isomers **25a**, **25b**. Fractional crystallization of this mixture from pentane gave *meso*-5,5,12,12-tetramethoxy-1,2,8,9-cyclotetradecatetraene (**25b**), mp 142–143°; ms *m/e* 308 (M^+, 8%), 293 ($M^+ - CH_3$, 2%), 277 ($M^+ - CH_3O$, 4%), 276 ($M^+ - CH_3OH$, 4.5%), 261 ($M^+ - C_2H_7O$, 8%), 245 ($M^+ - C_2H_7O$, 17%), 227, 213, 155, 123 (100%), 101, 97, 91, 88, 79, 77, 67, 65, 43; ir (KBr) 2950, 2830, 1970, 1456, 1325, 1304, 1269, 1250, 1207, 1192, 1149, 1109, 1067, 1055, 1028, 1001, 972, 903, 874, 864, 811, and 710 cm^{-1}; nmr 4.94–5.22 (m, 4 H, allene), 6.83 (s, 6 H, OCH_3), 6.85 (s, 6 H, OCH_3), 7.43–8.40 (m, 12 H, CH_2).

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.64; H, 8.92.

The combined filtrates were reduced to small volume by evaporation, and the resulting solution was separated by ptlc on silica, eluting with pentane–ether (85:15). Crystallization from pentane gave *rac*-5,5,12,12-tetramethoxy-1,2,8,9-cyclotetradecatetraene (**25a**): mp 107–108°; ms *m/e* 308 (M^+, 10%), 293 ($M^+ - CH_3$, 4%), 277 ($M^+ - CH_3O$, 6%), 276 ($M^+ - CH_4O$, 6%), 261 ($M^+ - C_2H_7O$, 10%), 245 ($M^+ - C_2H_7O_2$, 17%), 227, 213, 155, 123 (100%), 101, 97, 91, 88, 79, 77, 67, 65, 43; ir (KBr) 2950, 2830, 1960, 1460, 1437, 1360, 1327, 1286, 1259, 1211, 1190, 1110, 1073, 1066, 1053, 1030, 995, 920, 906, 890, 863, 803, 756, 745, and 709 cm^{-1}; nmr 4.56–5.13 (m, 4 H, allene), 6.84 (s, 12 H, OCH_3), 7.40–8.46 (m, 12 H, CH_2).

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.33; H, 9.13.

Hydrolysis of the Mixture of 25a and 25b. Preparation of Racemic (26a) and Meso (26b) 3,4,10,11-Cyclotetradecatetraene-1,8-diones. The mixture (154 mg, 0.5 mmol) of **25a**, **25b** was dissolved in acetone (5 ml), *p*-toluenesulfonic acid (5 mg), water (5 drops) and boron trifluoride etherate (1 drop) were added, and the mixture was shaken for 10 min. The solvent was removed by evaporation, the solid residue was extracted with ether (100 ml), and the ethereal solution was washed with water (5 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a mixture (90 mg, 83%) of the isomers **26a**, **26b**. Ptlc of the mixture on silica, eluting with pentane–ether (1:1), gave the following.

(i) *meso*-**3,4,10,11-Cyclotetradecatetraene-1,8-dione** (**26b**) (42 mg, 40%): mp 151–152° (pentane); ms *m/e* 216 (M^+, 5%), 198 ($M^+ - H_2O$, 10%), 188 ($M^+ - CO$, 3%), 187, 174, 173, 161, 159, 146, 121, 120, 119, 117, 107, 79 (100%); ir (KBr) 2975, 2800, 1970, 1710, 1415, 1370, 1352, 1263, 1219, 1092, 1026, 885, 835, and 695 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 224 nm sh (ε 825), 284 (330).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.30; H, 7.26.

(ii) *rac*-**3,4,10,11-Cyclotetradecatetraene-1,8-dione** (**26a**) (39 mg, 37%): mp 114–115°; ms *m/e* 216 (M^+, 5%), 198 ($M^+ - H_2O$, 2%), 188 ($M^+ - CO$, 4%), 187, 174, 173, 161, 159, 146, 121, 120, 119, 117, 107, 79 (100%); ir (KBr) 2940, 2860, 1960, 1710, 1445, 1424, 1415, 1395, 1370, 1300, 1258, 1152, 1120, 1068, 1048, 985, 885, 760, 727, and 705 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 223 nm sh (ε 700), 276 (190).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.46.

Hydrolysis of **25a** under the same conditions gave **26a** (75%), and similarly hydrolysis of **25b** gave **26b** (75%). The most convenient synthesis of **26a** and **26b** is from the mixture.

Hydrogenation of 26a and 26b. Compound **26a** (or **26b**) (216 mg, 0.1 mmol) was dissolved in ethyl acetate (5 ml), and this solution was added to prereduced platinum dioxide (20 mg) in ethyl acetate (1 ml), and the mixture was stirred under an atmosphere of hydrogen for 30 min. The catalyst was removed by filtration, and the filtrate was evaporated to give a crystalline solid. Crystallization from pentane gave cyclotetradeca-1,8-dione (16.5 mg, 74%), mp 148–149° (lit.[17] 147–148°). Reaction of cyclotetradeca-1,8-dione with hydroxylamine hydrochloride gave the corresponding dioxime (70%), mp 236–237° (lit.[17] 234–235°). The spectral data for both compounds were in accord with the assigned structures.

Partial Asymmetric Synthesis of 25a and 26a. The tetrabromide **24** (157 mg, 0.25 mmol) and (−)-sparteine (351 mg, 1.5 mmol) were added to ether (25 ml), and the mixture was stirred and cooled to −80° under N_2. Methyllithium (0.75 ml, 2 *M*, 1.5 mmol) was added in one portion and the reaction mixture allowed to warm to −10° and stirred for a further 30 min. Water (2 ml) was added, the ethereal layer was separated, and the aqueous phase was extracted with ether (10 ml). The combined ethereal extracts were washed with sulfuric acid (5%, 2 × 5 ml) and saturated $NaHCO_3$ (2 × 5 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a mixture of **25a** and **25b**, which was separated by ptlc on silica as described previously. The isomer **25a**, mp 105–107°, had an optical rotation, $[\alpha]^{20}D$ +12.20 ± 0.05° (*c* 10.5 g/100 ml, *n*-hexane), whereas **25b**, mp 142–143°, was optically inactive.

Hydrolysis of the mixture before separation, by the method described previously, gave a mixture of **26a** and **26b**. These were separated as previously described, and the isomer **26a**, mp 112–113°, was found to have an optical rotation, $[\alpha]^{20}D$ +34.10 ± 0.05° (*c* 0.97 g/100 ml, EtOH). The isomer **26b** was optically inactive.

Preparation of *cis,cis*- (23) and *cis,trans*- (24) 3,9-Cyclododecadiene-1,7-dione and *cis,cis*- (28) and *cis,trans*- (29) 3,10-Cyclododecadiene-1,7-dione. The solvent from the mother liquors obtained after the separation of **21** from the reduction of 5,5,11,11-tetramethoxy-1,2,7,8-cyclododecatetraene (**5**) with sodium–liquid ammonia (see above) was removed by evaporation to give an oil (1.4 g). The oil was dissolved in acetone (50 ml), *p*-toluenesulfonic acid (50 mg), water (1 ml), and boron trifluoride etherate (5 drops) were added, and the mixture was shaken for 10 min. The solvent was removed by evaporation and the residue was extracted with ether (100 ml). The ethereal extract was washed with water (5 ml) and dried ($MgSO_4$) and the solvent was removed by evaporation. The resulting solid was separated by ptlc on silica, eluting with pentane–ether (1:2), to give the following.

(i) *cis,cis*-**3,10-Cyclododecadiene-1,7-dione** (**28**) (100 mg, 5%), colorless oil: ms *m/e* 192 (M^+, 27%), 173 ($M^+ - H_2O$, 5%), 174 ($M^+ - CO$, 5%), 138, 110, 97, 96, 95, 81, 68, 67, 55, 54, 53, 41, 39 (100%); ir (film) 3020, 2930, 2860, 1705, 1655, 1460, 1435, 1362, 1300, 1265, 1203, 1140, 980, 960, 793, and 743 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 211.5 nm (ε 1700), 287 (130).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.47; H, 8.32.

(ii) *cis,trans*-**3,9-Cyclododecadiene-1,7-dione** (**27**) (240 mg, 12.5%): mp 57–58° (pentane–ether); ms *m/e* 192 (M^+, 10.5%), 174 ($M^+ - H_2O$, 0.3%), 164 ($M^+ - CO$, 3%), 138, 110, 109, 96, 92, 82, 81, 68, 67, 55, 54, 53, 41, 39 (100%); ir (KBr) 3030, 2940, 2860, 1700, 1660, 1450, 1419, 1374, 1335, 1308, 1260, 1229, 1210, 1173, 1139, 1108, 1030, 985, 939, 911, 812, and 708 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 211 nm (ε 1800), 291 (220).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.96; H, 8.34.

(iii) *cis,trans*-**3,10-Cyclododecadiene-1,7-dione** (**29**) (200 mg, 10%, see discussion): mp 69–70° (ether–pentane); ms *m/e* 192 (M^+, 50%), 174 ($M^+ - H_2O$, 8%), 164 ($M^+ - CO$, 6%), 149, 138, 110, 97, 96, 95, 93, 92, 81, 68, 67, 55, 54 (100%), 53, 41, 39; ir (KBr) 2960, 2930, 1700, 1660, 1635, 1450, 1434, 1407, 1352, 1278, 1228, 1140, 1100, 1091, 1068, 1040, 1000, 987, 960, 901, 880, 862, 846, and 710 cm^{-1}; nmr (see discussion); λ_{max}^{EtOH} 212 nm (ε 1900), 290 (150).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.57; H, 8.34.

(iv) *cis,cis*-**3,9-Cyclododecadiene-1,7-dione** (**23**) (120 mg, 6.5%), mp 118–119°, was identical in all observed respects with the previously described sample.

Ozonolysis of Compound 27. The diene **27** (48 mg, 0.25 mmol) was dissolved in absolute ethanol (10 ml), and ozone (3%, 1 l. min^{-1}) was bubbled through the solution for 45 min. The solution was then flushed with O_2 (5 min), sodium borohydride (0.5 g) was added in one portion, and the solution was heated under reflux for 15 min. After the solution was cooled, hydrochloric acid (3 *N*) was slowly added to the solution until all gas evolution ceased and the inorganic salts had dissolved. The solvents were removed by evaporation and acetic anhydride (7.5 ml) was added, and the mixture was heated to reflux for 15 min. The solvent was removed by evaporation, the residue was extracted with ether (25 ml), and the ethereal solution was dried ($MgSO_4$). Evaporation of the solvent and ptlc of the residue on silica, eluting with pentane–ether, gave

hexane-1,3,6-triol triacetate (75 mg, 61%), identical in all observed respects with the previously described sample.

Ozonolysis of Compound 28. The diene **28** (12 mg, 0.06 mmol) was dissolved in absolute ethanol (5 ml), ozonized, reduced (0.1 g of $NaBH_4$), and acetylated (2.5 ml of acetic anhydride) in an identical manner to compound **27**. A mixture of products was obtained, none of which corresponded to hexane-1,3,6-triol triacetate.

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Regiospecificity in Di-π-methane Photoisomerizations

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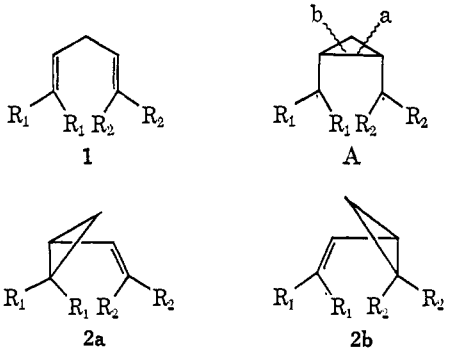
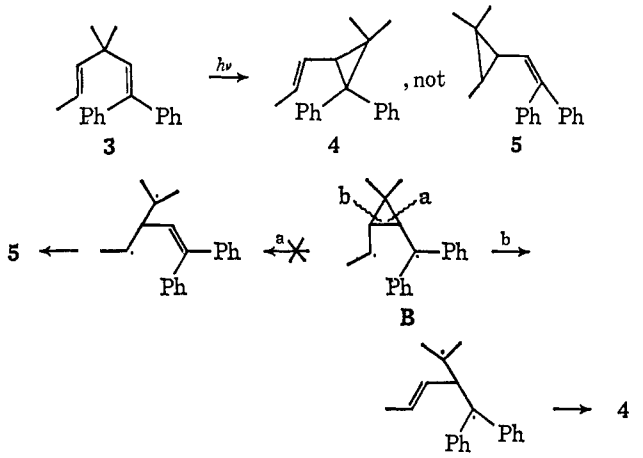
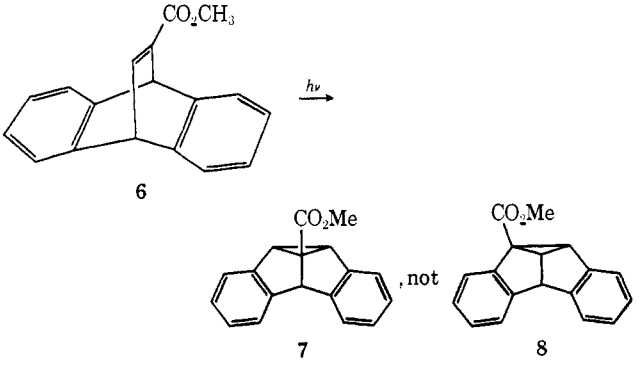
Abstract: The acetone-sensitized di-π-methane rearrangement of benzobicyclo[2.2.2]octadienes is affected by substituents in the saturated bridge, although these substituents are not bonded to any of the atoms directly involved in the rearrangement. For example, *syn*- and *anti*-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols **26s** and **26a** rearrange regiospecifically to **27s** and **27a**, respectively. Products arise preferentially from diradicals in which the unpaired electrons are close to (**31p**) rather than remote from (**31d**) the substituents (OH or OAc) on the saturated bridge. Since in several examples (**9**, **12**, **17**) the extent of regioselectivity depends on the geometry of the substituent, being greater when the substituent and aryl ring are syn, the interaction between the substituent and the unpaired electrons probably occurs through space, rather than through bonds.

The generality of the di-π-methane photorearrangement was first recognized by Zimmerman.[1] The reaction involves the conversion of a divinylmethane moiety **1** to a vinylcyclopropane **2**.[2] In cases when $R_1 \neq R_2$, two products (**2a** and/or **2b**) are possible, depending upon whether bond a or bond b is broken when intermediate A is converted to a stable product.[3] Several cases are known in which the reaction follows only one of these two possible routes. For example, direct irradiation of **3** gave **4**, not **5**.[5] Thus the "intermediate" B cleaved exclusively at bond b.





Another type of regiospecificity has been observed in bicyclic systems.[6] Irradiation of **6** gave **7**, not **8**. In this case, the mode of initial bonding determines the structure of the reaction product. The observed product arose from intermediate C, not D.



Each of these types of regiospecificity can be easily rationalized. The reactions proceed along routes which

(1) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967); for a thorough review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, in press.

(2) The term π is used in the broadest sense, and examples which involve aryl or carbonyl groups as components of the di-π-methane moiety are well known.

(3) For convenience in the discussion, A–F, etc., are represented as discrete intermediates. In some instances, such discrete diradicals may in fact be involved; in other cases, the reactions may be concerted.[4]

(4) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); P. S. Mariano and J.-k. Ko, *ibid.*, **94**, 1766 (1972); H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **94**, 5504 (1972), and leading references therein.

(5) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970).

(6) E. Ciganek, *ibid.*, **88**, 2882 (1966).