line products obtained from acid-catalyzed condensations of 4-alkyl-6-hydroxymethylguaiacols. This class of 1,2,4-trisubstituted cyclotribenzylenes appears to adopt only the flexible "saddle" conformation in contrast to CTV (2,3 disubstituted) which is locked in the "crown" conformation. This represents the first example of conformational control by aryl substitution pattern in the cyclotribenzylene system.

Experimental Section

The reaction mixtures were fully acetylated (pyridine–acetic anhydride 1:1 v/v) prior to pmr or glc analyses. Pmr spectra were normally recorded on a Varian HA-100 spectrometer using CDCl$_3$ as solvent and TMS as internal reference. The low-temperature experiments were recorded on a Varian XL-100 instrument in CD$_2$Cl$_2$ with 10% TMS. Glc analyses were obtained from a Varian Model 1520 gas chromatograph using a 6 ft × $^1/_8$ in. stainless steel column packed with 5% SE-30 coated on Chromosorb W (60–80 mesh). The column was temperature programmed from 90 to 250° at 6°/min and then held isothermally. The nitrogen carrier-gas flow rate was 20 ml/min. The injector port was maintained at 230° and flame-ionization detection was used. Ir spectra (KBr pellet) were recorded on a Perkin-Elmer 521 spectrophotometer. Low-resolution mass spectra were run on a MS-12 spectrometer. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

Cyclization.—6-Hydroxymethyl-4-methylguaiacol (1) and 6-hydroxymethyl-4-propylguaiacol (2) were prepared by the procedure of Marton, *et al.*,[15] and their purity checked by pmr spectroscopy. Cyclization was effected by heating 2 g of 1 or 2, 20 ml of water, and 7.5 ml of concentrated HCl under reflux for 2 hr. The reaction mixture was neutralized, extracted with ether, dried (Na$_2$SO$_4$), and evaporated (reduced pressure) to a syrup. After acetylation the reaction product was crystallized from ethanol. 10,15-Dihydro-1,6,11-triacetoxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**3a**) (0.61 g, 27%) had mp 280–282°; ν_{max} 1745, 1585, 1445, 1352, 1300, 1120, 1090, 1000, 915, 870, and 820 cm^{-1}; M$^+$ 576; retention time 51 min.

10,15-Dihydro-1,6,11-triacetoxy-2,7,12-trimethoxy-4,9,14-tripropyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**4a**) (0.57 g, 25%) had mp 207–209°; ν_{max} 1745, 1585, 1440, 1352, 1295, 1165, 1090, 1010, 870, and 820 cm^{-1}; M$^+$ 660; retention time 91 min.

De-O-acetylation.—Compounds **3a** and **4a** were de-O-acetylated by treating them with excess LiAlH$_4$ in THF. After recrystallization from aqueous ethanol, **3** was obtained as white crystals, mp *ca.* 135° dec. Somewhat impure (rust color) **4** was obtained from **4a** and had a melting point range of >10° at *ca.* 190° dec. Pmr indicated only traces <5% of impurities.

10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**3**) had ν_{max} 3430, 1585, 1440, 1280, 1230, 1200, 1175, 1090, 1025, 905, and 820 cm^{-1}; M$^+$ 450.

10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-tripropyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**4**) had ν_{max} 3530, 3495, 1585, 1450, 1270, 1230, 1180, 1090, 1005, 900, and 820 cm^{-1}; M$^+$ 534.

Acknowledgments.—We thank L. Rozon and D. Watson for technical assistance in the preparation of these compounds, and Dr. Ian Armitage for helping to obtain the low-temperature pmr spectra at the University of British Columbia.

Registry No.—**1**, 7452-08-6; **1a**, 42214-44-8; **2**, 32359-71-0; **2a**, 42214-46-0; **3**, 42214-47-1; **3a**, 42214-48-2; **4**, 42214-49-3; **4a**, 42319-50-6.

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[15] J. Marton, T. Marton, S. K. Falkenhag, and E. Adler, *Advan. Chem. Ser.*, **No. 59**, 125 (1966).

Photochemical and Acid-Catalyzed Rearrangements of Tricyclo[4.4.2.0]dodecanones[1,2]

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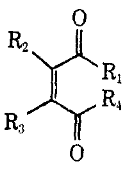
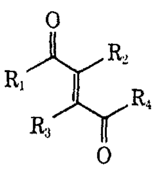
Photoannulations of transoid 2-ene-1,4-diones with ethylene and 2-butyne are described. An efficient synthesis of bicyclo[4.4.0]dec-1(6)-ene-2,7-dione (**7**) in two steps from 1,5-decalindiol has been accomplished. Acid-catalyzed and photochemical isomerizations of 11,12-dimethyltricyclo[4.4.2.0]dodec-11-ene-2,7-dione (**10**), the adduct of **7** and 2-butyne, are presented.

Although cycloaddition reactions of cisoid 2-ene-1,4-dione systems with acetylenes, olefins, and other enes are well documented,[3] the involvement of molecules containing transoid 2-ene-1,4-dione moieties in such reactions is not. In this paper we report that the latter enediones are effective partners in photocycloadditions with olefins and acetylenes.



cisoid 2-ene-1,4-dione



transoid 2-ene-1,4-dione

Irradiation of **1**[4] in hexane through uranium glass[5] at room temperature with 2-butyne very quickly and cleanly produced the β,γ-unsaturated dione **3**. Irradiation (Pyrex) of **1** at low temperature[6] in methylene chloride saturated with ethylene likewise gave a single adduct, **4** (Scheme I).

Since rearrangement studies with **3** and **4** would certainly be complicated by the presence of the angular methyl group, we required the parent enedione **7**. The electronic effect of the methyl group in methylfuran is apparently essential for conjugate addition to cyclohexenone to occur; thus furan could not be added to cyclohexenone under the same reaction conditions.

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[1] Presented in part by N. P. Peet at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 30, 1972, Abstract ORGN 86.

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

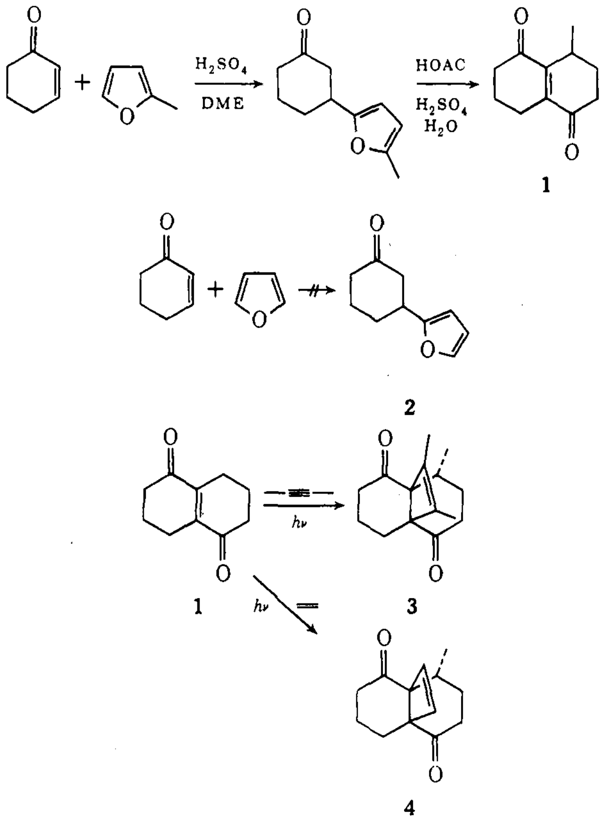
[3] Consider the number of examples in which quinones, benzoquinones, and maleic anhydrides have been used in photocycloaddition reactions: M. E. Kuehne and H. Linde, *J. Org. Chem.*, **37**, 4031 (1972); S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *ibid.*, **34**, 520 (1969); I. W. J. Still, M. W. Kwan, and G. E. Palmer, *Can. J. Chem.*, **46**, 3731 (1968); W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[4] M. A. Tobias, *J. Org. Chem.*, **35**, 267 (1970).

[5] When a Pyrex glass filter was employed in the preparation of **3**, two additional products were observed in the irradiation solution by glpc.

[6] The apparatus used for low-temperature irradiation was similar to that described by D. C. Owsley and J. J. Bloomfield, *J. Chem. Soc. C*, 3445 (1971).

SCHEME I

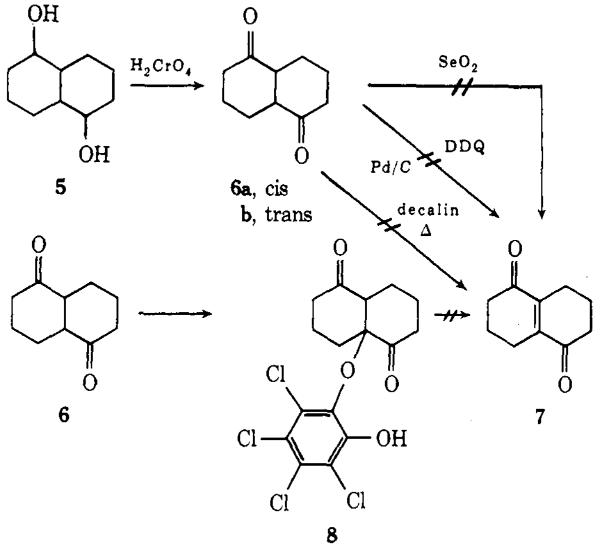


This negative result led us to explore alternate routes for the preparation of enedione **7**.

Enedione **7** is briefly mentioned only twice in the literature. Baumann and Prelog[7] reported its preparation in their laboratories by chloranil oxidation of 1,5-decalindione, but gave no experimental data. Campbell and Harris[8] report two oxidative processes for the production of **7** from $\Delta^{9,10}$-octalin, which gave overall yields of 3.5 and 0.5%.

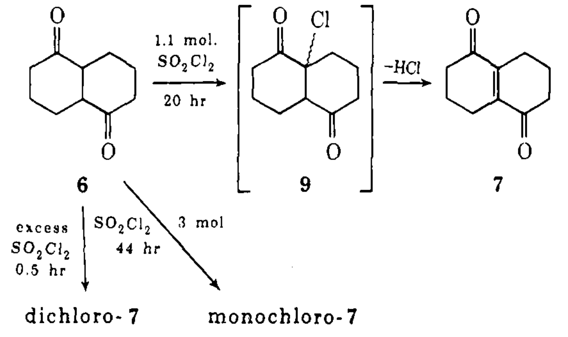
Commercially available 1,5-decalindiol (**5**) was converted into a mixture of *cis*- and *trans*-1,5-decalindiones (**6a** and **6b**, respectively) with Jones reagent.[9] Although selenium dioxide is reported to oxidize transoid 2-ane-1,4-diones to 2-ene-1,4-diones,[12] only trace amounts of **7** resulted from treatment of dione **6a** with selenium dioxide. Treatment of **6a** with 2,3-dichloro-5,6-dicyanoquinone (DDQ) yielded a small amount of **6b**, but no **7**. When **6a** was treated with 10% palladium on charcoal in decalin at reflux, dehydrogenation occurred but enedione **7** was not produced. Treatment of **6a** with *o*-chloranil in carbon tetrachloride gave a 52% yield of adduct **8**. Although treatment of **8** with base did yield a small amount of enedione **7** and provided supporting evidence for the structural assignment of adduct **8**, this did not constitute a practical synthesis of **7**. A probable side reaction of this base treatment is the abstraction of the phenolic proton followed by ether cleavage to regenerate *o*-chloranil and the enolate of **6**. Scheme II summarizes these unsuccessful routes to **7**.

SCHEME II



Treatment of **6** with sulfuryl chloride,[13] on the other hand, produced enedione **7** directly.[14] Treatment of **6** with excesses of sulfuryl chloride produced mono- and dichloro derivatives of **7** (Scheme III).

SCHEME III



Irradiation of enedione **7** with 2-butyne and ethylene (in the same manner as described for **1**) cleanly yielded the noval adducts **10** and **12**, respectively. Treatment of β,γ-unsaturated ketone **10** with *p*-toluenesulfonic acid (TsOH) in benzene at reflux rapidly produced the thermodynamically more stable enedione **11**, *via* a 1,2-vinyl shift followed by a Wagner–Meerwein shift.[15] Treatment of dione **12** with TsOH in the same manner resulted in two Wagner–Meerwein shifts[16] to produce dione **13** as the only product. Acid-catalyzed 1,3-acyl migration[15b,17] of **10** (*i.e.*, to product **14**) was

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(7) P. Baumann and V. Prelog, *Helv. Chim. Acta*, **42**, 736 (1959).

(8) W. P. Campbell and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 2721 (1941).

(9) 1,5-Decalindiol (Aldrich) was treated with 8 *N* chromic acid[10] to give a mixture of 1,5-decalindiones (93% yield). Fractional crystallization separated pure *cis*- and *trans*-1,5-decalindiones in yields of 41 and 33%, respectively. This preparation of **6** represents an improvement over previously used procedures.[11]

(10) D. C. Kleinfelter and P. v. R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

(11) W. S. Johnson, C. D. Gutsche, and D. K. Banarjee, *J. Amer. Chem. Soc.*, **73**, 5464 (1951).

(12) (a) C. S. Barnes and D. H. R. Barton, *J. Chem. Soc.*, 1419 (1953); (b) R. K. Hill, *J. Org. Chem.*, **26**, 4745 (1961).

(13) (a) A. J. Sisti and A. C. Vitale, *J. Org. Chem.*, **37**, 4090 (1972); (b) H. O. House and H. W. Thompson, *ibid.*, **26**, 3729 (1961).

(14) Chromatographic purification of **7** was necessary to free it of a minor impurity which could not be separated by recrystallization.

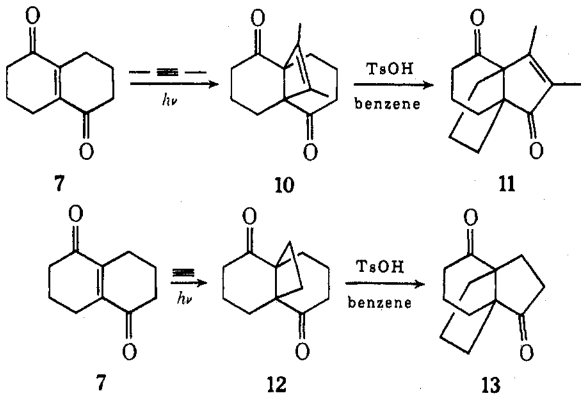
(15) (a) R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970); (b) R. L. Cargill, D. M. Pond, and S. O. Legrand, *ibid.*, **35**, 359 (1970), and references cited therein.

(16) N. P. Peet, R. L. Cargill, and D. F. Bushey, *J. Org. Chem.*, **38**, 1218 (1973).

(17) (a) R. L. Cargill, M. E. Beckham, J. R. Damewood, D. M. Pond, W. A. Bundy, and J. Bordner, *J. Org. Chem.*, **37**, 78 (1972); (b) R. L. Cargill and A. B. Sears, *Tetrahedron Lett.*, 3555 (1972); (c) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

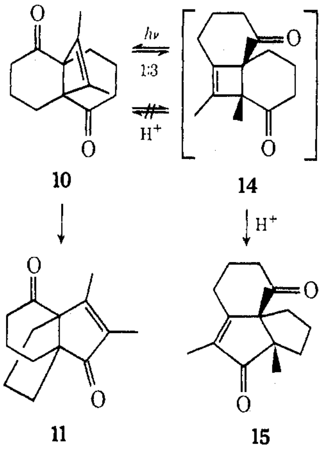
not observed (*vide infra*). The adducts of **7** and their rearrangements are summarized in Scheme IV.

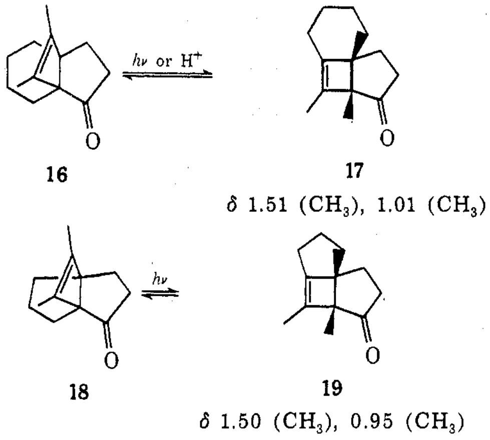
SCHEME IV



The ultraviolet spectrum of enedione **10** [299 nm (ϵ 472)] indicated efficient excited state mixing of olefinic and carbonyl orbitals (as was the case for enedione **3**) and we predicted that **10** would undergo a photochemical 1,3-acyl migration.[18-20] Irradiation (Pyrex) of **10** in hexane gave a mixture from which ketones **11** and **15** (Scheme V) were isolated by glpc in a 1:3 ratio, respectively. Analysis of the reaction mixture on another column led to isolation of **10** and **15** in a 1:3 ratio. (The initial column was then shown to isomerize **10** to **11**.) Analysis of the methyl region of the nmr spectrum of the reaction mixture before glpc indicated the presence of **10**, the absence of **15**, and methyl singlets at δ 1.57 and 1.10. The nmr spectra of ketones **17**[17c] and **19**,[17b] which are photoisomers of **16** and **18**, respectively, show methyl singlets in similar regions. An infrared spectrum of the reaction mixture indicated that the major component had a carbonyl stretching frequency of 1705 cm^{-1}. These data indicate the photochemical formation of **14**, and its subsequent isomerization to **15** during gas chromatography. Further analysis of the nmr spectrum of the photostationary mixture indicated the presence of **10** and **14** in a ratio of *ca.* 1:3.

SCHEME V





The structures of **14** and **15** follow from the body of knowledge already obtained in these laboratories regarding photochemical and acid-catalyzed isomerizations of propellane systems such as the ones under discussion,[15-17] coupled with the spectroscopic data already described. Isolation of pure **14** was unsuccessfully attempted using a variety of glpc columns. Thick layer chromatography (silica gel) of the irradiation mixture also failed to separate **14**.

Since treatment of **11** with TsOH in benzene at reflux yielded no trace of **15**, and since **15** treated in the same manner yielded no trace of **11**, we conclude that the formation of **14** in the irradiation of **10** was not an acid-catalyzed isomerization. This result is interesting in view of the fact that similar compound sets, **16** $\rightleftarrows$ **17** and **18** $\rightleftarrows$ **19**, are equilibrated under acidic conditions. Furthermore, when a portion of the photostationary mixture was treated with TsOH in benzene at reflux, the resulting mixture contained **11** and **15** in a ratio of 1:3, respectively. This result again demonstrates that the acid-catalyzed interconversion of **10** and **14** has a barrier which is greater than those leading from **10** to **11** and from **14** to **15**.

Experimental Section[21]

5-Methylbicyclo[4.4.0]dec-1(6)-ene-2,7-dione (1).—Enedione 1, mp 50–54° (lit.[4] mp 50–53.5°), was prepared in an overall yield of 13% from cyclohexenone.[4] Careful recrystallization of 1 (hexane) yielded a purer product, mp 58–60°, which was used in the subsequent reactions. Enedione 1 had mp 58–60°; ir (CCl_4) 1670 cm^{-1} (C=O); uv max (95% EtOH) 264 nm (ϵ 12,000); nmr ($CDCl_3$) δ 3.3–1.7 (m, 11, all protons except CH_3) and 1.17 (d, J = 7.2 Hz, 3, CH_3).

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(18) For recent references to photoisomerizations of this type in rigid systems, see K. E. Hine and R. F. Childs, *Chem. Commun.*, 145 (1972); H. Hart and A. F. Naples, *J. Amer. Chem. Soc.*, **94**, 3256 (1972); and R. L. Cargill and T. Y. King, *Tetrahedron Lett.*, 409 (1970).

(19) For recent reports of 1,3-acyl photoisomerizations in nonrigid β,γ-unsaturated ketones, see J. R. Williams and G. M. Sarkisan, *J. Chem. Soc. D*, 1564 (1971); P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 4357 (1972); and P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 9252 (1972).

(20) (a) N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, **38**, 1222 (1973); (b) R. L. Cargill, T. Y. King, and A. B. Sears, *ibid.*, **36**, 1423 (1971); (c) N. A. LeBel, N. D. Ojha, J. R. Menke, and R. J. Newland, *ibid.*, **37**, 2896 (1972); (d) K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, **94**, 6233 (1972).

(21) All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Infrared spectra were recorded using a Perkin-Elmer Model 257 grating spectrophotometer. All nmr spectra were determined using tetramethylsilane as an internal standard, with a Varian A-60 nmr spectrometer. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 instrument. Analytical gas-liquid partition chromatograms were determined using a Varian Aerograph 1200 flame ionization chromatograph, and preparative glpc separations were conducted using a Varian Aerograph 90-P-3 chromatograph. Irradiations were carried out using a Hanovia high-pressure mercury arc (450 W), internal probe, type L, with the filter specified.

Attempted Preparation of 3-(2-Furyl)cyclohexanone (2).—A mixture of 113 g (1.18 mol) of cyclohexenone (Columbia Organic), 104 g (1.53 mol) of furan (MCB), 575 ml of dimethoxyethane, and 1 ml of concentrated H_2SO_4 was heated at reflux for 24 hr. The dark solution was cooled and stirred (30 min) with $NaHCO_3$ (10 g). The excess $NaHCO_3$ was removed by filtration, and the filtrate was fractionally distilled at reduced pressure. Distillates consisted largely of recovered starting materials, with only a small amount of material in the boiling point range expected for a 1:1 adduct of furan and cyclohexenone, which was not **2** (or **7**).

5,11,12-Trimethyltricyclo[4.4.2.0]dodec-11-ene-2,7-dione (3).—A solution of 0.912 g (5.12 mmol) of enedione **1** and 20 ml of 2-butyne (Columbia Organic) in 150 ml of hexane was irradiated (uranium glass filter) for 2.75 hr. The disappearance of **1** and the appearance of a single product was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 150°, 30 cc/min of He). Removal of the solvent left 1.14 g (96%) of **3** as an oily solid. Adduct **3** was purified by elution through a 2-g plug of alumina[22] with hexane, followed by low-temperature recrystallization[23] (hexane) and sublimation [75° (0.35 mm)]. Adduct **3** had mp 80.5–82°; uv max (95% EtOH) 235 nm (ϵ 3500) and 302 (500); nmr ($CDCl_3$) δ 2.8–1.3 (m, 19, all protons except angular CH_3, with CH_3 multiplets at 1.61 and 1.50) and 0.84 (d, J = 7.2 Hz, 3, angular CH_3); mass spectrum (70 eV) m/e 232 (molecular ion).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.72; H, 8.73.

5-Methyltricyclo[4.4.2.0]dodecane-2,7-dione (4).—A solution of 0.971 g (5.12 mmol) of enedione **1** in 150 ml of CH_2Cl_2 saturated with ethylene (Matheson) was irradiated (Pyrex filter) at low temperature for 2.25 hr. Progress of the addition was followed by glpc (3% DEGS, 8 ft × 0.125 in., 140°, 30 cc/min of He). The reaction solution was warmed to room temperature and dried ($MgSO_4$), and the solvent was removed to leave 1.13 g (99%) of **4** as a viscous oil, which solidified upon standing. Separation of **4** from minor impurities was accomplished by preparative glpc (20% SE-30, 5 ft × 0.25 in., 210°, 85 cc/min of He). Adduct **4** had mp 72–74°; uv max 296 nm (ϵ 55); ir (CCl_4) 1695 cm^{-1} (C=O); nmr (CCl_4) δ 2.6–1.3 (m, 17, all protons except CH_3) and 0.88 (d, J = 7.2 Hz, 3, CH_3); mass spectrum (70 eV) m/e 206 (molecular ion).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.73; H, 8.84.

Bicyclo[4.4.0]dec-1(6)-ene-2,7-dione (7).—A solution of 2.08 g (12.5 mmol) of *trans*-1,5-decalindione (**6**)[9] and 1.81 g (13.4 mmol) of sulfuryl chloride (MCB) in 50 ml of CH_2Cl_2 was stirred for 20 hr. Progress of the reaction was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 120°, 30 cc/min of He). The yellow reaction mixture was neutralized with saturated $NaHCO_3$, the layers were separated, and the organic phase was dried ($MgSO_4$) and concentrated to leave 2.30 g of yellow solid. Recrystallization (hexane) yielded yellow material displaying a wide melting point range (85–100°) which was applied (CH_2Cl_2) to a 100-g column of alumina.[22] Elution with ether–hexane mixtures (1:9 to 1:1) afforded initial, intensely yellow fractions which were combined, concentrated, and recrystallized (hexane) in two crops to yield 0.738 g (36%) of **7** as yellow plates. Enedione **7** had mp 111–113° (lit. mp 110–111°[7] and 113–114°[8]); ir (CCl_4) 1680 cm^{-1} (C=O); uv max (95% EtOH) 265 nm (ϵ 12,000); nmr δ 2.7–2.3 (m, 8, CH_2 groups adjacent to C=O and C=C groups) and 2.3–1.7 (m, 4, remaining CH_2 groups); mass spectrum (70 eV) m/e 164 (molecular ion).

When a 1.04-g (6.25 mmol) quantity of **6b** was stirred with 2.81 g (20.8 mmol) of sulfuryl chloride in 50 ml of CH_2Cl_2 for 44 hr, the major product was monochloro-**7**. Progress of the reaction was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 135°, 30 cc/min of He). After 5 hr, the major product (95% by glpc) was **7**, and, after 44 hr, the major product (90% by glpc) was monochloro-**7**. Work-up of the reaction mixture as above yielded 1.37 g of oily, yellow solid which was recrystallized twice (ether–hexane and hexane) to yield 0.216 g of yellow prisms. Monochloro-**7** had mp 102–111°; ir (KBr) 1690 and 1675 (C=O), 1175, and 1155 cm^{-1}; mass spectrum (70 eV) m/e 198 (molecular ion).

When a 1.04-g (6.25 mmol) quantity of **6b** was stirred with 10 ml of sulfuryl chloride (neat) for 30 min, the major product (70% by glpc) was dichloro-**7**. (The remaining 30% was monochloro-**7**.) Work-up of the reaction mixture as above yielded 1.58 g of yellow solid which was recrystallized twice ($CHCl_3$–hexane and $CHCl_3$–ether) to yield 0.413 g of white solid which displayed a single peak on glpc (3% DEGS, 8 ft × 0.125 in., 150°, 30 cc/min of He). Dichloro-**7** had mp 153–156°; ir (KBr) 1690 (C=O) and 1155 cm^{-1}; mass spectrum (70 eV) m/e 232 (molecular ion).

Attempted Preparations of 7. Isolation of Adduct 8.—A 0.979-g (5.89 mmol) quantity of **6a** in 50 ml of absolute ethanol and 2.40 g (5.89 mmol) of selenium dioxide (MCB) were heated at reflux for 90 min. The reaction mixture was filtered, concentrated, and eluted through a plug of alumina[22] (ether). The eluent was concentrated and the residue was recrystallized (heptane) to yield 0.6 g of **6b**. An infrared spectrum of the concentrated mother liquor indicated the presence of a small amount of enedione **7**. The use of an acetic acid–hexane solvent system and excess selenium dioxide afforded no trace of **7**.

A 0.866-g (5.21 mmol) quantity of **6a**, 0.5 g of 10% palladium on carbon (Columbia Organic), and 25 ml of *cis*- and *trans*-decalin (MCB) were heated at reflux for 1.5 hr, during which time 150 ml of gas was evolved. (Theoretical gas evolution volume for conversion to enedione is *ca.* 115 ml.) The reaction mixture was cooled and filtered, and the concentrated filtrate was applied to a 25-g column of alumina.[22] Elution with ether and CH_2Cl_2 removed 0.712 g of white solid. Recrystallization (CH_2Cl_2–hexane) afforded 0.451 g of **6b**.

A 1.04-g (6.25 mmol) quantity of **6a** and a 1.52-g (6.69 mmol) quantity of 2,3-dichloro-5,6-dicyanoquinone[24] in 50 ml of benzene were heated at reflux for 1 hr. The red reaction solution was concentrated and applied to a 50-g column of alumina.[22] The column was eluted with ether to remove a small amount of **6b**.

A 0.954-g (5.74 mmol) quantity of **6a** and 1.46 g (5.95 mmol) of *o*-chloranil (Columbia Organic) in 50 ml of CCl_4 were stirred for 3 hr. The initially clear, red solution deposited a voluminous precipitate after 3 hr which was removed by filtration and washed with CCl_4 to yield 1.22 g (52%) of adduct **8**, which was recrystallized from ether: mp 240–242° dec; ir (KBr) 3650–3100 (OH), 1695 (C=O), 1590, and 1425 cm^{-1}. The material was not soluble in available nmr solvents. Adduct **8** exhibited a positive ferric chloride test.[25] When a small amount of **8** was slurried with ether and dilute KOH, the ether layer became yellow. Concentration of the ether phase gave a yellow solid whose infrared spectrum was identical with that of enedione **7**.

Anal. Calcd for $C_{16}H_{14}Cl_4O_4$: C, 46.63; H, 3.42; Cl, 34.41. Found: C, 46.76; H, 3.41; Cl, 34.41.

11,12-Dimethyltricyclo[4.4.2.0]dodec-11-ene-2,7-dione (10).—A solution of 1.01 g (6.16 mmol) of enedione **7** and 10 ml of 2-butyne in 150 ml of hexane was irradiated (uranium glass filter) for 1.3 hr. Progress of the addition was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 135°, 30 cc/min of He). Removal of the solvent left 1.38 g of clear oil which solidified on standing. The material was eluted through a 2-g plug of alumina[22] with ether–hexane and recrystallized (hexane) at low temperature[23] to yield 0.818 g (61%) of **10**. A sample was sublimed [70° (0.15 mm)] for elemental analysis. Adduct **10** had mp 71–75°; ir (CCl_4) 1690 cm^{-1} (C=O); uv max (95% EtOH) 230 nm (ϵ 3640) and 299 (472); nmr (CCl_4) δ 2.4–1.6 (m, 12, all protons except CH_3 groups) and 1.54 (s, 6, CH_3 groups); mass spectrum (70 eV) m/e 218 (molecular ion).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.88; H, 8.26.

8,9-Dimethyltricyclo[4.3.3.0]dodec-8-ene-2,7-dione (11).—A solution of 0.213 g (0.974 mmol) of **10** and 0.5 g of *p*-toluenesulfonic acid monohydrate (Baker, $TsOH \cdot H_2O$) in 45 ml of benzene was heated at reflux for 1.5 hr with azeotropic removal of water. Analysis of reaction solution aliquots by glpc (3% DEGS, 8 ft × 0.125 in., 130°, 30 cc/min of He) indicated that rearrangement was complete in less than 15 min. The cool reaction mixture was washed with saturated $NaHCO_3$ (30 ml) and water (30 ml), dried ($MgSO_4$), and concentrated to leave 0.167 g (79%) of **11**. To separate it from minor impurities originally present,[26] **11** was collected from glpc (20% SE-30, 5 ft × 0.25 in., 185°, 85 cc/min of He) as a clear oil. Enedione **11** had ir (CCl_4) 1700 (C=O groups) and 1645 cm^{-1} (C=C); uv max (95%

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[22] Baker aluminum oxide (pH of 10% slurry at 25° 7.8) was used.

[23] Low-temperature recrystallization was accomplished by suspending the solution in a dewar flask containing Dry Ice and capped with a loose fitting plug.

[24] Prepared by J. L. Moore using the method of D. Walker and T. D. Waugh, *J. Org. Chem.*, **30**, 3240 (1965).

[25] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1956, p 127.

[26] Compound **10** partially deteriorated, upon standing for 3 weeks, to an oily solid.

EtOH) 247 nm (ϵ 10,300) and 296 (476); nmr (CCl_4) δ 2.4–1.0 (m, all protons, with CH_3 singlets at 1.90 and 1.72); mass spectrum (70 eV) *m/e* 218 (molecular ion).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.02; H, 8.22.

Tricyclo[4.4.2.0]dodecane-2,7-dione (12).—A solution of 0.886 g (5.39 mmol) of enedione **7** in 150 ml of CH_2Cl_2 saturated with ethylene was irradiated (Pyrex filter) at low temperature[27] for 1.5 hr. Progress of the addition was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 135°, 30 cc/min of He). The reaction solution was dried ($MgSO_4$) and the solvent was removed to leave 1.11 g of clear oil which solidified upon standing. The material was eluted through a 2-g plug of alumina[22] with ether–hexane and recrystallized (hexane) at low temperature[28] to yield 0.707 g (68%) of **12**. A portion of **12** was sublimed [60° (0.15 mm)] for elemental analysis. Adduct **12** had mp 45–48°; ir (CCl_4) 1705 cm^{-1} (C=O); uv max (95% EtOH) 296 nm (ϵ 59); nmr (CCl_4) δ 2.5–1.2 (m); mass spectrum (70 eV) *m/e* 192 (molecular ion).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.91; H, 8.22.

Tricyclo[4.3.3.0]dodecane-2,7-dione (13).—A solution of 0.076 g (0.395 mmol) of **12** and 0.5 g of $TsOH \cdot H_2O$ in 45 ml of benzene was heated at reflux for 1 hr with azeotropic removal of water. Progress of the rearrangement was monitored by glpc (3% DEGS, 8 ft × 0.125 in., 135°, 30 cc/min of He). The cool reaction mixture was washed with saturated $NaHCO_3$ (30 ml) and water (10 ml), dried ($MgSO_4$), and concentrated to leave 0.070 g (92%) of **13**. Dione **13** was collected from preparative glpc (20% SE-30, 5 ft × 0.25 in., 170°, 85 cc/min of He) for characterization: mp 115–118°; ir (CCl_4) 1740 (cyclopentanone C=O) and 1705 cm^{-1} (cyclohexanone C=O); uv max (95% EtOH) 292 nm (ϵ 42); nmr (CCl_4) δ 2.5–1.2 (m); mass spectrum (70 eV) *m/e* 192 (molecular ion).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.92; H, 8.27.

Preparation of Transient 2,3-Dimethyltricyclo[6.4.0.0^{3,8}]dodec-1-ene-4,9-dione (14) and Its Acid-Catalyzed Conversion to 1,3-Dimethyltricyclo[7.3.0.0^{4,9}]dodec-3-ene-2,8-dione (15).—A 0.814-g (4.96 mmol) quantity of enedione **7** was converted to adduct **10** as described, using a base-washed irradiation vessel. The uranium glass filter was removed and irradiation (Pyrex) was continued for 3.75 hr, until glpc (3% DEGS, 8 ft × 0.125 in., 135°, 30 cc/min of He) indicated a mixture of static integral intensity numbers. Collection of the smaller of the two major peaks (present in *ca.* a 1:3 ratio) from glpc (10% Apiezon M, 8 ft × 0.25 in., 220°, 85 cc/min of He) showed it to be enedione **11**, which had been formed from enedione **10** on the column. [This was proved by collection of **10** from another glpc system (20% SE-30, 5 ft × 0.25 in., 180°, 85 cc/min of He) which did not cause this conversion.] Collection of the larger peak yielded enedione **15**: bp 100° (0.2 mm); ir (CCl_4) 1705 (C=O) and 1650 cm^{-1} (C=C); uv max (95% EtOH) 251 nm (ϵ 7890), 221 (4470), and 315 (305); nmr (CCl_4) δ 3.0–1.0 (m, with CH_3 singlets at 1.71 and 1.07); mass spectrum (70 eV) *m/e* 218 (molecular ion).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.09; H, 7.90.

The finding that **14** was a labile precursor of **15** and the determination of the photostationary mixture of **10** and **14** (as 1:3, respectively) are presented in the discussion section.

Registry No.—**1**, 22242-82-6; **3**, 42249-31-0; **4**, 42245-83-0 **6a**, 42245-84-1; **6b**, 42245-85-2; **7**, 42245-86-3; monochloro-**7**, 42249-11-6; dichloro-**7**, 42249-12-7; **8**, 42245-87-4; **10**, 42245-88-5; **11**, 42245-89-6; **12**, 42245-90-9; **13**, 42245-91-0; **14**, 42245-92-1; **15**, 42245-93-2; cyclohexenone, 930-68-7; 2-butyne, 503-17-3; ethylene, 74-85-1.

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[27] Low temperature was maintained by immersing the irradiation vessel in a Dry Ice–isopropyl alcohol bath, and circulating isopropyl alcohol, cooled indirectly with Dry Ice, through the probe.

Photochemical Addition of Dimethyl Maleate to 2,3-Dimethyl-2-butene. Use of a Chiral Shift Reagent

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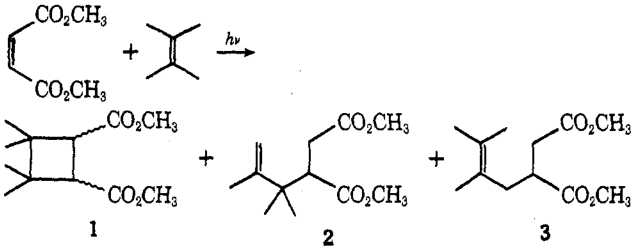
Irradiation (253.7 nm) of dimethyl maleate with excess 2,3-dimethyl-2-butene gave dimethyl (1,1,2-trimethylallyl)succinate (49% of product), dimethyl (2,3-dimethyl-2-butenyl)succinate (33%), and dimethyl 3,3,4,4-tetramethylcyclobutane-*trans*-1,2-dicarboxylate (18%) in 33% yield. The stereochemistry of the cyclic ester was proven by conversion to the corresponding cis ester by way of the cyclic anhydride. Proton nmr spectra of the trans ester with added tris(trifluoroacetylcamphorato)europium showed different shifts for the hydrogens of the enantiomers in the racemic modification of the compound; the corresponding cis (meso) ester, similarly treated, showed different shifts for the enantiotopic nuclei, the differential shifts being intramolecular as shown by coupling between the nonequivalent methine hydrogens in the shifted spectra.

In spite of the increasing number of ways in which instrumental methods can be applied to problems of structure elucidation, chemical degradations and even independent syntheses of degradation products are frequently necessary in difficult structure problems. In connection with another problem we recently required authentic samples of *cis*- and *trans*-3,3,4,4-tetramethylcyclobutane-1,2-dicarboxylic acid, and in the process of identifying these compounds practiced a recently proposed instrumental method that promises great savings in time and material as compared with traditional chemical methods.

The dimethyl ester (**1**) of one of the desired acids was produced, albeit as a minor product, by irradiation of a mixture of dimethyl maleate and 2,3-dimethyl-2-butene (tetramethylethylene, TME). The structures of the other products, **2** and **3**, were determined unambiguously by instrumental methods (see Experimental Section) and are consistent with the allylic abstraction–radical recombination mechanism proposed for the photoaddition of dimethyl maleate to cyclohexene[2] that was confirmed by labeling studies.[2d] Only a single isomer of **1** was produced in this reaction;



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[2] (a) P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc., London*, 54 (1963); (b) J. A. Barltrop and R. Robson, *Tetrahedron Lett.*, 597 (1963); (c) P. de Mayo, *Pure Appl. Chem.*, **9**, 597 (1964); (d) G. Ahlgren and B. Åkermark, *Tetrahedron Lett.*, 1885 (1970).