hexoxide being oxidized at very nearly the same potential as is required for **2** or **3**. Addition of cyclohexanol to a solution of the tosylate did not eliminate the B peak, in contrast to the effect of methanol on the B peak of methyl tosylate. Instead, there was a very slight shift of peak potential in the anodic direction, indicative of the slightly less cathodic oxidation potential of cyclohexoxide as compared with that of **2** or **3**. Addition of cyclohexoxide caused the B peak to increase without affecting the rest of the signal. Addition of methanol eliminated the cyclohexoxide peak, as expected.

The authors intend to investigate further the behavior of very easily oxidized anions. However, they expect to use a system other than tosylate because the mixture of products produced causes undesirable voltammetric complexity.

Experimental Section

Reagents.—Acetonitrile was prepared according to the procedure previously described.[9] Commercial tetraethylammonium bromide was recrystallized from methanol and dried under a vacuum at 80°. Tetrapropylammonium perchlorate was prepared from the iodide as previously described by Kolthoff.[10]

Methyl, ethyl, neopentyl, and cyclohexyl tosylates were prepared according to the procedure of Tipson.[11] Our experimental melting points agreed with literature values for the following: cyclohexyl tosylate, 44°: methyl tosylate, 28°; ethyl tosylate, 32°;[12] neopentyl tosylate, 48°.[13] *n*-Butyl tosylate was Eastman White Label.

Dicyclohexyl ether, with a boiling point of 244° (lit.[14] bp 239–240°), was prepared by a hydrogen–Raney nickel reduction of phenylcyclohexyl ether in cyclohexane solution at 175° and 30 atm. Other reagents were the best available grade, used without purification.

Cyclic Voltammetry.—Cyclic voltammetry curves were obtained on the apparatus previously described.[15] Sweep rates were 10 V/sec, with a 3-m/sec step width. The microelectrode was a mercury-plated platinum wire. A silver–0.10 *M* $AgNO_3$–acetonitrile reference electrode was used for all electrolyses. Voltammetric curves were recorded using unthermostated cells in a room having ambient temperature at 22°.

Constant Potential Electrolyses.—Electrolyses were performed with a conventional three-electrode potentiostat. All electrolysis cells were constructed to permit use of vacuum-line techniques for solution handling. Large-scale electrolyses were performed in H cells with either mercury pool or glassy carbon cathodes and silver or platinum anodes. Solutions were degassed by repeated freezing and pumping and were then stored under a nitrogen or a helium atmosphere.

Product Analyses.—Reaction vessels were fitted with septums which allowed direct sampling of cathode solution or head space by a syringe. Alcohols, ethers, tripropylamine, propylene, methane, ethane, butane, cyclohexane, neopentane, and toluene were determined or sought by gas chromatography, on appropriate columns, on samples taken directly from the cathode compartment. In all cases, valid samples of compounds of interest were chromatographed for comparison. This applies also to compounds sought but not found, *e.g.*, methane after methyl tosylate reduction; care was taken to ascertain that these would be seen, if present, considering the interferences present in the samples analyzed.

Toluene and *p*-toluenesulfinate ion were detected by ultraviolet absorption spectroscopy.

Mercury analyses were performed on reaction mixtures with a Perkin-Elmer Model 290 atomic absorption spectrometer.

Acknowledgment.—The authors wish to acknowledge financial support from the National Institutes of Health through Grant GM-10064.

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[9] J. F. O'Donnell, J. T. Ayers, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

[10] I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 870 (1957).

[11] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[12] R. S. Tipson, M. A. Clapp, and L. H. Cretchen, *ibid.*, **12**, 133 (1947).

[13] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

[14] H. Willstatler, *Chem. Ber.*, **45**, 1466 (1912).

[15] C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).

The Tetramers of Acetylenedicarboxylic Esters[1]

J. C. Kauer and H. E. Simmons

Contribution No. 1384 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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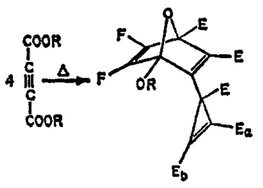
Dimethyl and diethyl acetylenedicarboxylate form thermal tetramers which have been characterized as cyclopropenyl derivatives of oxanorbornadiene **1a** and **1b**. Various degradative reactions verify this structural assignment. The hexadeuterated tetramer analog **1c** was synthesized by trapping the reactive cyclopropenylfuran **10a** with dimethyl acetylenedicarboxylate-d_6. The tetramer of the methyl ester undergoes photochemical reaction to form semibullvalene derivative **13**.

The dimethyl[2,3] and diethyl esters of acetylenedicarboxylic acid spontaneously react to form tetrameric products. From spectral studies Le Goff and LaCount have recently proposed the cyclopropenyloxanorbornadiene structure **1a** for the crystalline methyl ester **1a**.[3] The chemical and spectral studies here reported verify this assignment. The tetrameric ethyl ester which exhibits similar infrared and ultraviolet spectra is assigned analogous structure **1b**.



1a, E = F = $COOCH_3$; R = CH_3
b, E = F = $COOC_2H_5$; R = C_2H_5
c, E = $COOCH_3$; F = $COOCD_3$; R = CH_3

Spectral Features.—The tetramers and several of their derivatives described below exhibit medium intensity absorptions at 1870–1900 cm^{-1} in their infrared and Raman spectra. Absorptions in this region are characteristic of the highly substituted cyclopropene ring system,[4] although compounds containing conju-

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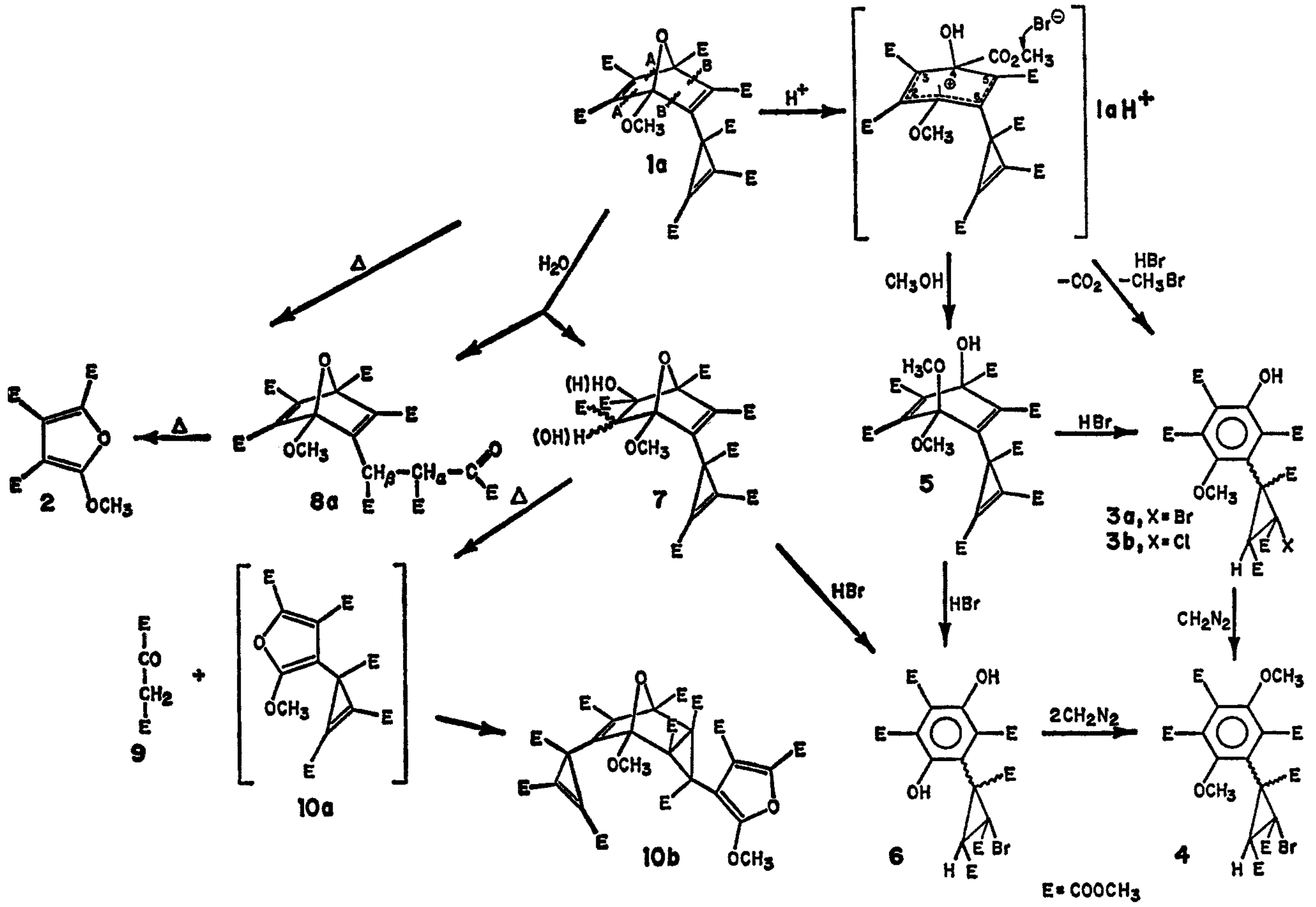
[1] Presented in part at the Third Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968.

[2] (a) M. J. Goldstein, private communication. (b) G. L. Thayer, Jr., Thesis, Cornell University, 1965, p 89 ff; *Dissertation Abstr.*, **26**, 104 (1965).

[3] E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2333 (1967).

[4] (a) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966); (b) *ibid.*, **1**, 115 (1966).

SCHEME I
RING-OPENING REACTIONS OF THE TETRAMER OF DIMETHYL ACETYLENEDICARBOXYLATE



gated allenic[5] linkages, cyclopropanones,[6] or cyclopropenones[4b] also exhibit such absorptions.

The nmr spectrum of tetramer **1a** in acetone-d_6 exhibits eight distinct and equal methoxyl resonances. (The synthesis of the hexadeuterated analog **1c** described below permits the rational assignment of two of these peaks.) Somewhat poorer separation of the eight peaks is observed in acetonitrile-d_3 and benzonitrile, whereas in chloroform and bromoform two of the peaks coalesce to form a sharp singlet, leading to the seven-line spectrum reported by Le Goff and La Count.[3] When the bromoform solution is warmed to 135–150°, the peaks again separate, and a well-resolved eight-line spectrum is obtained.

At first glance, structure **1a** might be considered to be incompatible with the observed eight-line nmr spectrum. The cyclopropene ring is attached to an asymmetric system, however, and even with free rotation around the bond connecting it with the oxanorbornadiene moiety, the methoxycarbonyl groups E_a and E_b are at all times in different magnetic environments. Similar chemical-shift differences for *gem*-dimethyl (and other) groups adjacent to asymmetric systems have often been observed.[7]

Although the tetramers exhibit a strong, broad absorption "tail" in the ultraviolet region between 200 and 250 mμ, careful studies using either purified acetonitrile or isooctane solvent in a 1-mm cell indicate no absorption maximum above 200 mμ. A distinct shoulder at 225 mu (ε *ca.* 17,000) is observed, however, in both **1a** and **1b**.[8a] The absorption intensity at 205 mμ (ε 18,000) in acetonitrile is in reasonable agreement with the presence of three *cis*-1,2-bis(methoxycarbonyl)ethylene (or acrylic ester) chromophores in the tetramer molecule. By comparison, dimethyl maleate exhibits very similar end absorption in this region.[8b]

Chemical Properties of the Tetramer.—As Le Goff and LaCount[3] have pointed out, the tetramer is very sensitive to base, and attempts to hydrolyze the ester with aqueous base rapidly extinguish the cyclopropene absorption.[9]

Although the tetramer **1a** possesses three double bonds, attempts at direct bromination, even in the presence of bromide ion, were unsuccessful. Catalytic hydrogenation produced an ill-defined mixture of hydrogenation products which could not be separated. The dienophilic reactivity of the cyclopropene double bond in **1a** has been noted by other workers.[2,3]

Strong support for structure **1a** comes from the pyrolysis of the tetramer and from several ring-

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 62.

(6) See, for instance, N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **87**, 2774 (1965).

(7) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

(8) (a) Le Goff and LaCount[3] report λ_{max}^{EtOH} 220 mμ (ε 15,500), 232 shoulder (ε 12,600) for **1a**; Thayer[2b] reports no absorption maximum above 220 mμ. We prefer to avoid the use of hydroxylated solvents because of the reaction of **1a** with both water and methanol (see below). (b) R. F. Rekker, P. J. Brombacher, H. Hamann, and W. T. Nauta [*Rec. Trav. Chim.*, **73**, 410 (1954)] report for dimethyl maleate λ_{max}^{EtOH} 205 mμ (log ε 3.90). We find no real peak above 200 mμ in acetonitrile solvent; at λ^{CH_3CN} 205 mμ, ε = 7000.

(9) Careful treatment of the ester with 7 equiv of aqueous barium hydroxide at 25° produces a yellow barium salt. Acidification with the calculated amount of sulfuric acid produces a solid, water-soluble acid, which on treatment with diazomethane yields an intractable methyl ester having no cyclopropene absorption.

opening reactions which lead to easily crystallized products. These reactions are summarized in Scheme I.

Pyrolysis.—When the tetramer is heated to 180° under reduced pressure, some dimethyl acetylenedicarboxylate is obtained as well as 2-methoxy-3,4,5-tris(methoxycarbonyl)furan (2). The latter is identical in all its properties with the product recently reported by other laboratories.[2,10] This reaction provides strong evidence that a 7-oxanorbornene residue is present in the molecule; cleavage of the molecule (a reverse Diels–Alder reaction) at bonds B–B (Scheme I) would yield the furan whereas similar cleavage at A–A would produce dimethyl acetylenedicarboxylate. The other pyrolysis products were not characterized. This reverse Diels–Alder reaction to produce the furan 2 was found to be generally useful to verify the presence of the 7-oxanorbornadiene (or 7-oxanorbornene) moiety in the derivatives described below.

Reaction of the tetramer **1a** with anhydrous hydrogen bromide in benzene gives a phenolic monobromide **3a**. This can occur by protonation of the oxygen bridge of **1a** to produce the stabilized carbonium ion **1a**-H$^+$ (Scheme I). Attack by bromide ion at the methyl of the methoxycarbonyl group in the 4 position could lead to direct aromatization of the six-membered ring. Such displacements have precedence in solvents such as benzene, where bromide ion (or its solvates or complexes) is known to be very nucleophilic.[11] Addition of hydrogen bromide to the cyclopropene ring ultimately produces the cyclopropyl bromide **3a**, which reacts with 1 mol of diazomethane to give the dimethyl ether **4**.

The tetramer **1a** also reacts with hydrogen chloride to form the monochloride **3b**, whose infrared, ultraviolet, and nmr spectra are nearly superimposable on those of the bromide **3a**.

Methanolysis.—Tetramer **1a** reacts with methanol in the presence of a trace of hydrogen chloride to form the stable ketal **5** in 42% yield. Here again, protonation of the oxygen bridge can produce the carbonium ion **1a**-H$^+$ which is attacked by methanol at the 1-carbon atom. Cyclopropene (1880 cm^{-1}) and hydroxyl (3550 cm^{-1}) absorptions are prominent in the infrared spectrum of **5**, and the nmr spectrum shows one hydroxyl and nine methoxyl groups. Seven of the latter resonances occur between δ 3.65 and 3.86 ppm downfield from tetramethylsilane in acetone-d_6, typical positions for ester or vinyl methoxyl groups, and two occur at δ 3.10 and 3.18 ppm, typical of methoxyl groups attached to saturated carbon atoms. The ultraviolet spectrum of **5** suggests the presence of three *isolated* 1,2-bis(methoxycarbonyl)ethylene (or acrylic ester) chromophores[8b] and rules out structures having conjugated double bonds (*e.g.*, those resulting from attack by methanol on ion **1a**-H$^+$ at positions 3 or 5). The ketal **5** is cleaved by hydrogen bromide to form the methoxyphenol **3a**, as well as the corresponding hydroquinone **6**. The latter is converted by diazomethane into the dimethyl ether **4**, identical with that obtained from **3a**. As expected, pyrolysis of **5** at 180° did not give the furan **2**.

Hydration.—The tetramer reacts slowly in 50% aqueous dioxane to form approximately equal amounts of two hydrates, **7**, mp 126° (26%), and **8a**, mp 147° (25%). The reaction, which can be followed by thin layer chromatography, is virtually complete after 10 days at 25°.

The higher melting hydrate does not exhibit the typical cyclopropene absorption in the infrared region. Addition of water to the cyclopropene ring of **1a** followed by cleavage produces the partially enolized β-keto ester **8a**. On pyrolysis of **8a** at 170°, furan **2** was obtained, verifying the presence of the oxanorbornadiene ring system. The only peak in the uv spectrum of **8a** ($\lambda_{\max}^{\mathrm{EtOH}}$ 260 mμ, ϵ 12,080) shows a bathochromic shift when sodium hydroxide is added to its ethanol solution ($\lambda_{\max}^{\mathrm{EtOH}}$ 270 mμ, ϵ 14,000). The enolic nature of the product, suggested by its ready solubility in warm, aqueous potassium bicarbonate, is verified by its nmr spectrum in which both the keto and enol forms can be distinguished.

At 25° in chloroform-*d*, the proportion of the enol is about 70% as determined by the $H_{\beta E}$ and $H_{\beta K}$ resonances at δ 4.58 and 4.71 ppm, respectively. This assignment was verified by the synthesis of the deuterium analog **8b** by treatment of **1a** with deuterium oxide followed by exchange with water. The nmr spectrum of **8b** was essentially superimposable on that of **8a**, except that the resonances assigned to $H_{\beta K}$ and $H_{\beta E}$ were absent.

The lower melting hydrate has been assigned structure **7**, which arises from the addition of water to one of the oxanorbornadiene double bonds of **1a**. The presence of the intact cyclopropene ring is indicated by the infrared absorption at 1882 cm^{-1}. The nmr spectrum in acetone-d_6 exhibits eight well-resolved methoxyl resonances as well as a nonexchangeable single proton absorption assigned to tertiary C–H and an exchangeable hydroxyl resonance. The ultraviolet spectrum is similar to those of the parent tetramers **1a** and **1b**; however, the intensity of the absorption (at $\lambda^{\mathrm{CH_3CN}}$ 200 mμ, ϵ 10,900) suggests only two maleic or acrylic ester residues.[8b]

On treatment with hydrogen bromide, **7** is converted in good yield into the hydroquinone **6**. Pyrolysis of **7** at *ca.* 140° (0.3 μ) produces in good yield two fission products, dimethyl oxalacetate (**9**) and a crystalline solid dimer of the furan **10a** (the furan **2** was not detected). The formation of **9** indicates that the less hindered double bond of the oxanorbornadiene ring of **1a** is involved in the hydration reaction; however, the direction of the addition cannot be deduced from these results. Evidence for the intermediacy of the cyclopropenyl furan **10a** is described below. This furan is the intermediate which Le Goff and La Count[3] propose in the thermal tetramerization of dimethyl acetylenedicarboxylate.

We tentatively assign structure **10b** to the dimer. The infrared spectrum indicates the presence of a cyclopropene moiety. Twelve methoxyl resonances appear in the nmr spectrum. One of these, far upfield, is assigned to the bridgehead methoxyl, and the other eleven

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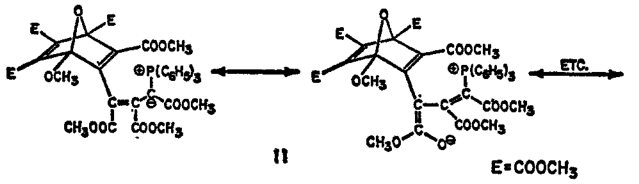
(10) This compound has been reported to be present among the products of the liquid phase pyrolysis[2,10a,b] and copper-catalyzed[10c] decomposition of dimethyl acetylenedicarboxylate. It seems probable that the tetramer **1a** is the actual intermediate which leads to this furan. (a) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Lett.*, 1185 (1966). (b) T. Fukunaga, private communication. (c) E. Winterfeldt and G. Giesler, *Angew. Chem.*, **78**, 588 (1966.

(11) I. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **30**, 1076 (1964); *Chem. Abstr.*, **62**, 5160*e* (1965). *Cf.* H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.*, **74**, 3570 (1952).

are grouped in the region in which ester, vinyl, or aryl methoxyls are normally observed.

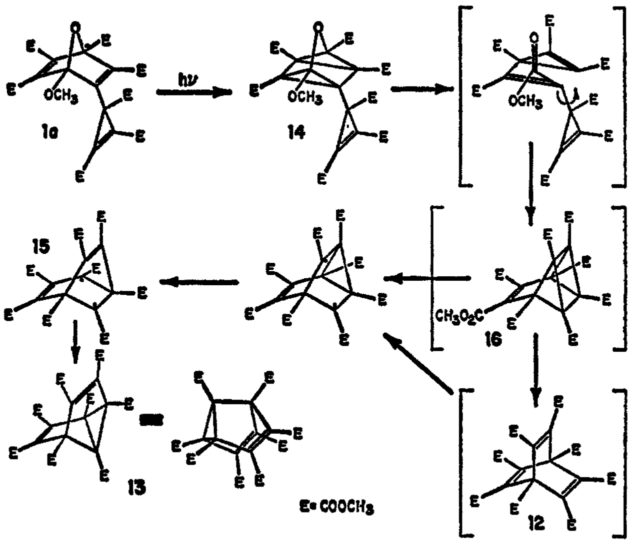
Reaction with Triphenylphosphine.—The aromatization of cyano-substituted oxanorbornadienes with triphenylphosphine has been reported by Weis.[12] In an attempt to employ this reaction to degrade the tetramers, ether or benzene solutions of **1a** and triphenylphosphine were mixed at room temperature, and a deep red color was immediately produced. When the solution was allowed to stand or was diluted with pentane, a red, crystalline 1:1 adduct, mp 213–214°, was obtained in high yield. The absence of the 1880–1900-cm^{-1} infrared absorption indicates that the cyclopropene ring has reacted, but the oxanorbornadiene ring appears to be intact, since the furan **2** is obtained on heating the red adduct above its melting point. Attack by triphenylphosphine to form the ylide **11** is suggested.



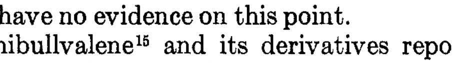
Delocalization of the charge over the long conjugated system could account for the deep color.[13]

Photochemistry.—Irradiation of **1a** in ether or tetrahydrofuran gives a photoisomer which melts at 163° and whose nmr spectrum in chloroform-*d* exhibits two methoxyl resonances in a ratio of 3:1. The larger peak is noticeably unsymmetrical and splits into two peaks in a ratio of 1:2 in acetone-d_6. The resulting three-peak 1:2:1 spectrum is clearly not consistent with the barrelene **12** tentatively suggested by other workers.[3] In addition, the ultraviolet spectrum of the photoisomer suggests the presence of only two bis(methoxycarbonyl)-ethylene residues.[8b] On these grounds we suggest the semibullvalene structure **13** for the photoisomer. The ultraviolet absorption maximum (225 mμ, ε 12,400) is at slightly longer wavelength than that of most maleic ester derivatives (195–212 mμ),[8b] indicating that the two chromophores may interact weakly with each other or with the cyclopropane ring.[14] Semibullvalenes have been reported to arise from the photolysis of barrelene and its derivatives.[15] By a minor modification of the reasonable mechanism suggested by Le Goff and LaCount[3] we can account for the formation of **13** (Scheme II). Irradiation of **1a** is expected to give the oxaquadricyclane **14**, a reaction which has been demonstrated recently for oxanorbornadienedicarboxylic ester derivatives.[16] Cleavage of **14**, perhaps photochemically, can ultimately lead to the diradical **15** by either of the pathways indicated. Zimmerman and coworkers[14b] have recently provided evidence for the intermediacy of such allylic diradicals in the formation of semibullvalene from barrelene. The barrelene **12** or its valence isomer **16** may be involved in the reaction; however, we have no evidence on this point.

SCHEME II



In semibullvalene[15] and its derivatives reported to date, it has not been possible to "freeze out" the bond fluctuation A ⇆ B by cooling. When a solution of **13** in acetone-d_6 was cooled to −90°, no broadening of the 1:2:1 proton nmr spectrum was detected. A 1:2:2:2:1 pattern would be expected if the A ⇆ B fluctuation became slow with respect to the nmr time scale.



Formation of the Tetramers of Acetylenedicarboxylic Ester.—Both the ethyl and methyl esters of acetylenedicarboxylic acid slowly undergo the tetramerization reaction at 25°. The rate of conversion is *ca.* 3% per year even when light is excluded. After several years, the solution of the methyl ester is supersaturated. Crystallization of **1a** can be induced by seeding, and two interconvertible crystalline modifications, mp *ca.* 105 and 115°, respectively, can be isolated. We did not succeed in crystallizing the ethyl analog **1b**, although it can be purified by column chromatography.

The reaction rate is greatly increased at elevated temperatures; however, **1** decomposes above its melting point. We find that, for a laboratory preparation of **1a**, a good compromise between rate and yield is reached at 85°. Under these conditions **1a** may be isolated in 20–25% conversion after 10–11 days merely by seeding the reaction mixture; the yield based on the dimethyl acetylenedicarboxylate is *ca.* 50%.

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(12) C. D. Weis, *J. Org. Chem.*, **27**, 3520 (1962).

(13) A. N. Hughes and M. Woods [*Tetrahedron*, **23**, 2973 (1967)] report that 2-methoxy-3,4,5-tris(methoxycarbonyl)furan (**2**) reacts with triphenylphosphine in ether at room temperature to give a red 2:1 adduct ($C_{40}H_{39}O_{16}P$), mp 215–217°. We observe no reaction under their conditions between carefully purified furan (**2**) and triphenylphosphine. We do find that much **1a** is produced by both procedures which they describe for the preparation of **2**. Since their red adduct has nearly the same melting point, elemental composition, and uv and nmr spectra as **11** ($C_{42}H_{39}O_{16}P$), it seems probable that their product is identical with **11** and arises from contamination of their furan sample with **1a**.

(14) (a) Y. Yukawa, "Handbook of Organic Structural Analysis," W. A. Benjamin, Inc., New York, N. Y., 1965, p 44. (b) G. Schröder [*Chem. Ber.*, **97**, 3131 (1964)] reports that homotropilidenes with a similar arrangement of parallel double bonds absorb at *ca.* 232 mμ (ε 3000–6000).

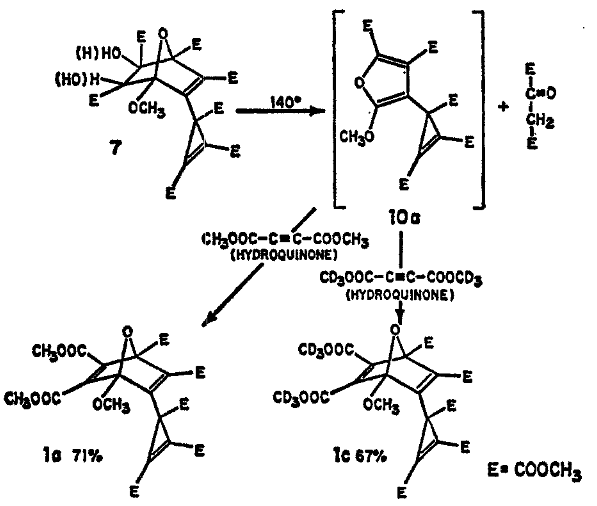
(15) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) R. S. H. Liu, *ibid.*, **90**, 215 (1968).

(16) (a) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem.*, **78**, 1057 (1966); (b) E. Payo, L. Cortes, J. Montacon, C. Rivas, and G. de Pinto, *Tetrahedron Lett.*, 2415 (1967).

We did not find any catalysts which would significantly increase the rate of formation of **1**, although several typical free-radical inhibitors (*e.g.*, hydroquinone, phenothiazine) in trace quantities markedly slowed the reaction. When the tetramerization is attempted in the presence of 0.15 mol of hydroquinone (100° for 3 days), little or no tetramer is formed and a 1:1 adduct with hydroquinone (**17**) is isolated. A radical-chain mechanism might explain these results.

The mechanism proposed by Le Goff and LaCount[3] involves initial 1,3-dipolar addition of dimethyl acetylenedicarboxylate with itself to produce a carbenoid intermediate which in turn reacts with a third mole of acetylenedicarboxylic ester to give the cyclopropenylfuran **10a**. The latter undergoes a conventional Diels–Alder reaction to form **1a**. That the cyclopropenylfuran **10a** is unusually reactive was suggested by studies of the pyrolysis of **7** at 140°. Under these conditions, the presumed intermediate furan **10a** was converted completely into the dimer **10b**. Therefore, two experiments to trap the furan **10a** were carried out. (1) A mixture of **7** with excess dimethyl acetylenedicarboxylate and hydroquinone was heated to 140° for 1 hr. The tetramer **1a** was formed, presumably from the reaction of **10a** with the acetylene, and no **10b** was isolated. In a control experiment, dimethyl acetylenedicarboxylate and hydroquinone gave little or no **1a** under similar conditions. (2) The pyrolysis of **7** was carried out in the presence of excess hexadeuteriodimethyl acetylenedicarboxylate, and the hexadeuterated tetramer analog **1c** was isolated in 67% yield. These experiments verify that the very reactive furan **10a** is formed from **7** at 140° and that it reacts readily with dimethyl acetylenedicarboxylate under these conditions to form the tetramer **1a** (Scheme III). The feasibility of the last step of the Le Goff–LaCount mechanism is thus established.

Scheme III



Experimental Section[17]

All melting points are corrected. Nmr spectra were obtained with a Varian A-60 spectrometer. Saturated chloroform-*d* or acetone-d_6 solutions with tetramethylsilane as an internal standard were used as noted. Peak center positions are reported as δ_H (parts per million) downfield from tetramethylsilane; number of protons (by integration) is given in brackets. Infrared spectra were determined in potassium bromide wafers with a Perkin-Elmer 21 spectrophotometer unless otherwise noted. Prominent peaks are noted: s = strong, m = medium, w = weak, b = broad, v = very.

Tetramer of Dimethyl Acetylenedicarboxylate. Tetramethyl 4-Methoxy-5[1,2,3-tris(methoxycarbonyl)-2-cyclopropen-1-yl]-7-oxabicyclo[2.2.1]hepta-2,5-diene-1,2,3,6-tetracarboxylate (1a).—Freshly distilled dimethyl acetylenedicarboxylate (209 g) was heated for 10 days in an oil bath maintained at 85°. The viscous, amber, oily product was poured into a covered crystallizing dish, seeded, and allowed to crystallize for 4 days. It was suction filtered in a sintered-glass funnel. The crystals (36 g) were twice triturated with *ca.* 100 ml of ether and then with a small smount of methanol and were sucked dry. The filtrate and the ether washes were combined and seeded with **1a**. Hexane (*ca.* 60 ml) was added dropwise over a period of several hours to obtain a second crop of 12.5 g. The white, crystalline product was essentially pure **1a**. The filtrate was vacuum distilled, and 111 g of dimethyl acetylenedicarboxylate was recovered. The yield of tetramer **1a** was 49%.

A portion of the product was recrystallized from methanol to give fine white needles: mp 103.5–105°; λ^{CH_3CN} (no maximum >200 mμ) 205 mμ (ε 18,000), 225 shoulder (15,800), 235 (11,400), 250 (5660); ν_{max}^{KBr} 3030 (w), 2980 (m), 2860 (w), 1880 (m), 1740–1720 (s), 1630 (m), 1440 (s), 1320 (s), 1260 (b,s), 1213 (s), 1140 (s), 1062 (s), 1014–1008 (m), 983 (w), 966 (w), 945 (w), 920 (w), 904 (m), 855 (w), 824 (w), 826 (m), 813 (w), 784 (m), 758 (m), 734 (w), 723 cm^{-1} (m); the Raman spectrum in chloroform (4558 Å excitation) exhibited strong peaks at 2955, 1890, 1730, 1650, and 1450 cm^{-1}; nmr (acetone-d_6) δ 3.590 [3], 3.647 [3], 3.715 [3], 3.763 [3], 3.827 [3], 3.853 [3], 3.862 [3], 3.935 [3]. The solubility of this product in the following solvents was measured at 28° (solvent, solubility in grams of solute per 100 ml of solvent): dichloromethane, 133; acetonitrile, 125; chloroform, 91; dioxane, 56; benzene, 22; tetrahydrofuran, 20; methanol, 2.1; diethyl ether, 0.2.

A second crystalline modification, mp 113–115°, was obtained by evaporation of a chloroform solution of **1a**. This modification could be obtained as large, well-formed prisms from 1:1 acetonitrile–xylene. The infrared spectra of both crystalline modifications were identical in solution.

Tetramer of Diethyl Acetylenedicarboxylate. Tetraethyl 4-Ethoxy-5-[1,2,3-tris(ethoxycarbonyl)-2-cyclopropen-1-yl]-7-oxabicyclo[2.2.1]hepta-2,5-diene-1,2,3,6-tetracarboxylate (1b).—A 30-g sample of freshly distilled diethyl acetylenedicarboxylate was heated in an oil bath to 85° for 11 days, The unreacted ester was carefully distilled under reduced pressure, bp 46° (0.18 mm), using a bath temperature of 80°. The viscous, amber, oily residue weighed 9.50 g. (A 48-g sample of diethyl acetylenedicarboxylate was allowed to stand at 25° for 3.5 years. When similarly distilled, it yielded 8.8 g of oily residue of somewhat better purity than that obtained by the thermal process.)

The above oil (1 g) was chromatographed on a silicic acid column using methylene chloride as eluent. The center fractions exhibited uniform infrared spectra. The viscous, oily product was vacuum dried for 7 days: λ^{CH_3CN} 220 mμ shoulder (ε 17,000) (no maximum >200 mμ); ν_{max} (oil) 2980 (s), 1875 (m), 1730 (vs), 1655 (w), 1630 (m), 1470 (m), 1448 (m), 1395 (m), 1372 (s), 1312 (b,s), 1258 (b, vs), 1175 (m), 1140 (b,s), 1095 (mw), 1060 (m), 1025 (b,s), 917 (b,w), 853 (b, m), 842 cm^{-1} (b,w).

Anal. Calcd for $C_{32}H_{40}O_{16}$: C, 56.46; H, 5.92. Found: C, 56.19; H, 5.98.

Pyrolysis of Tetramer 1a. 2-Methoxy-3,4,5-tris(methoxycarbonyl)furan (2).—**1a** (30 g) was heated to 100° (0.1 mm) in a sublimation apparatus connected to a vacuum pump through a liquid nitrogen-cooled trap. After 5 hr, 1.75 g of dimethyl acetylenedicarboxylate was obtained from the trap, and 2.04 g of crude, white, crystalline sublimate **2** was isolated. The pot residue weighed 25.0 g.

The crude **2** was sublimed at 105° (0.03 mm) and the sublimate was recrystallized from benzene–hexane to yield colorless crystals: mp 118.0–119.2° (lit. mp 117–118,[10a] 121°[10c]); λ_{max}^{EtOH} 275 mμ (ε 14,500), 245 shoulder (8910) [lit.[10c] 273 (15,400), 248 sh (10,900)]; nmr (chloroform-*d*) δ 3.82 [3], 3.92 [3], 3.97 [3], 4.26 [3] (lit.[10c] δ 3.83 [3], 3.88 [3], 3.98 [3], 4.28 [3], calculated from reported τ values); ν_{max} 3010 (w), 2950 (m), 1760–1717 (s), 1606 (s), 1584 (s), 1490 (ms), 1464 (m), 1432 (ms), 1412 (ms), 1360 (m), 1327 (s), 1253–1243 (s), 1187 (ms), 1147 (s), 1105

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[17] We wish to thank Miss E. Wallace for determining the Raman and ultraviolet spectra of the compounds reported and Miss N. Schlichter for the infrared spectra. We wish to thank Dr. G. S. Reddy for the 100-Mc nmr studies of the photolysis product **13**. Deuterium analyses were done by J. Nemeth, Urbana, Ill.

(s), 1061 (s), 997 (m), 950 (m), 815 (s), 786 (s), 768 (w), 727 (m), 666 (w) (lit.[10c] 1750, 1620, 1590, 1160, 1110, 1070 cm^{-1}). Compound **2** was also obtained by the pyrolysis of compounds **8** and **11** at 180°.

Reaction of 1a with Hydrogen Bromide. Trimethyl 3-Hydroxy-6-methoxy-5[2-bromo-1,2,3-tris(methoxycarbonyl)cyclopropyl]trimellitate (3a).—A solution of 30 g of **1a** in 300 ml of benzene was cooled to 10°, and dry hydrogen bromide was bubbled through for 10 min. The solution was allowed to stand for 30 min at room temperature, and dry nitrogen was then bubbled through the solution for 30 min to remove excess hydrogen bromide. (Methyl bromide was identified in the volatile fraction by mass spectrometry.) Solvent was removed under reduced pressure and 30 ml of methanol was added to the residual oil. After 3 days, the yellow crystalline precipitate (9.9 g) was filtered off and washed with methanol. An additional 5.5 g was obtained from the filtrates; the total yield of **3a** was 49%. A portion of the product was twice recrystallized from methanol[18] to give very light yellow crystals: mp 147–148.4°; $\lambda_{\max}^{\mathrm{EtOH}}$ 336 mμ (ϵ 7330) 255 sh (6100); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 330 mμ (ϵ 7560) 252 sh (6550), 209 (28,900); $\nu_{\max}$ 3500 (vw), 3000 (w), 2950 (m), 2840 (w), 1745 (vs), 1680 (m), 1605 cm^{-1} (m); nmr (benzene), δ 3.39 [3], 3.49 [3], 3.52 [3], 3.55 [4], 3.62 [3], 3.77 [3], 3.99 [3], 11.47 [1].

Anal. Calcd for $C_{22}H_{23}O_{14}Br$: C, 44.68; H, 3.89; Br, 13.52. Found: C, 44.73; H, 3.85; H, 13.44.

This analysis was checked by high-resolution mass spectroscopy using an Associated Electronic Industries MS-9 spectrometer (for peak at 590 mass units, 590.0279[19] (calcd 590.0272).

Reaction of 1a with Hydrogen Chloride. Trimethyl 3-Hydroxy-6-methoxy-5[2-chloro-1,2,3-tris(methoxycarbonyl)cyclopropyl]trimellitate (3b).—A solution of 20 g of **1a** in 150 ml of benzene was saturated with hydrogen chloride and held at room temperature for 5 days. Solvent and excess hydrogen chloride were removed under reduced pressure. The residue in methylene chloride was washed with water and dried ($MgSO_4$). Solvent was removed under reduced pressure and the residue was crystallized from methanol.[18] The crude, white, crystalline product (6.55 g) was recrystallized from methanol to yield colorless crystals: mp 172.6–173.4°; $\lambda_{\max}^{\mathrm{EtOH}}$ 335 (ϵ 6890), 255 sh (5960); nmr (acetone-d_6) 3.22 [1], 3.73 [3], 3.83 [3], 3.85 [6], 3.91 [6], 3.97 [6].

Anal. Calcd for $C_{22}H_{23}O_{14}Cl$: C, 48.31; H, 4.24; Cl, 6.84. Found: C, 48.57; H, 4.20; Cl, 6.90.

Reaction of 1 with Methanol. Tetramethyl 3-Hydroxy-6,6-dimethoxy-5-[1,2,3-tris(methoxycarbonyl)-2-cyclopropen-1-yl]-cyclohexa-1,4-diene-1,2,3,4-tetracarboxylate (5).—A solution of 50 g of **1a** in 100 ml of dichloromethane was diluted with 1100 ml of methanol. A small amount (*ca.* 200 ml) of hydrogen chloride gas was bubbled through the solution. The solution was allowed to stand at room temperature for 5 days. Solvent was removed on a rotary evaporator using a water pump vacuum. The residue in dichloromethane was washed twice with water, dried ($MgSO_4$), concentrated, and crystallized from methanol[18] to yield 22.0 g (42%) of colorless crystals in four crops. A portion was recrystallized from methanol for analysis: mp 165.2–167.4°; $\lambda_{\max}^{\mathrm{EtOH}}$ 203 mμ (ϵ 20,700); $\nu_{\max}$ 3450 (m), 3030 (w), 2970 (m), 2860 (w), 1885, (m), 1755 (vs), 1685 (w), 1645 cm^{-1} (w); nmr (acetone-d_6) 3.10 [3], 3.18 [3], 3.65 [3], 3.67 [3], 3.71 [3], 3.73 [3], 3.79 [3], 3.82 [3], 3.86 [3], 5.13 [1] (exchanges with CF_3COOH).

Anal. Calcd for $C_{25}H_{28}O_{17}$: C, 50.00; H, 4.70. Found: C, 49.92; H, 4.98.

Hydrolysis of 1a. Separation of 7 and 8a.—A stirred solution of 106 g of **1a** in 2.5 l. of dioxane was slowly diluted with 2.5 l. of water. The course of the hydrolysis was followed by thin layer chromatography on silica gel "G" plates (E. Merck A.G., Darmstadt, Germany; plates made by Analtech, Inc., Wilmington, Del.). Using 1:1 acetone–hexane, R_f values of **1a**, **7**, and **8a** were *ca.* 0.6, 0.5, and 0.1, respectively. After 10 days, little or no **1a** could be detected. The solvent was evaporated at room temperature. The residue was dissolved in dichloromethane, dried ($MgSO_4$), and concentrated to obtain a viscous, yellow oil weighing 103.5 g.

A solution of 15.2 g of this oil in 25 ml of chloroform was chromatographed on a silica gel H column (E. Merck, Darmstadt, Germany, distributed by Brinkman Instruments Co., Westbury, N. Y.) with 40% acetone in hexane solvent to yield in the first fractions 6.0 g of crude **7**. This material was dissolved in 15 ml of acetone, and hexane was added to the cloud point. Colorless crystalline **7** (3.75 g, 25%) slowly deposited (see next section for properties).

The remaining 88.3 g of yellow oil was dissolved in 110 ml of methanol. The solution gradually deposited 26.6 g (26%) of **8a** (see below for properties).

Tetramethyl 2(3)-Hydroxy-1-methoxy-6-[1,2,3-tris(methoxycarbonyl)-2-cyclopropen-1-yl]-7-oxabicyclo[2.2.1]-hept-5-ene-2,-3,4,5-tetracarboxylate (7).—The crude crystalline **7** described in the preceding section was twice recrystallized from acetone–hexane to yield short prisms: mp 126–126.6°; no ultraviolet peak above 195 mμ was detected; $\lambda^{\mathrm{CH_3ON}}$ 200 mμ (ϵ 10,900), 230 (9860), 250 (7040); a shoulder appeared at 235 mμ (ϵ 9660) in ethanol solution; $\nu_{\max}$ 3470 (m), 3030 (w), 2950 (m), 2850 (w), 1882 (m), 1735 (vs), 1642 cm^{-1}; nmr (acetone-d_6) δ 3.56 [3], 3.62 [1], 3.64 [3], 3.67 [3], 3.71 [3], 3.75 [3], 3.79 [3], 3.94 [3], 3.98 [3], 5.07 [1] (exchanges with D_2O). The tertiary hydrogen resonance at δ 3.62 is shifted downfield of all the methoxyl peaks in benzene solvent.

Anal. Calcd for $C_{24}H_{26}O_{17}$: C, 49.15; H, 4.47. Found: C, 49.19; H, 4.46.

Tetramethyl 2-[3-Oxo-1,2,3-tris(methoxycarbonyl)propyl]-1-methoxy-7-oxabicyclo[2.2.1]hepta-2,5-diene-3,4,5,6-tetracarboxylate (8a).—The crude crystalline **8a** obtained from the hydrolysis of **1a** (see above) was twice recrystallized from methanol[18] to yield short, triangular prisms: mp 146.5–147.7°; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 258 mμ (ϵ 12,000), 215 shoulder (13,880); $\lambda_{\max}^{\mathrm{EtOH}}$ 260 (ϵ 12,080); $\lambda_{\max}^{\mathrm{EtOH}}$ (0.1 *N* NaOH) 270 (14,000); $\nu_{\max}$ (Nujol) 3530 (w), 1755–1730 (vs), 1685 (s), 1620 cm^{-1} (m); nmr (acetone-d_6 at 25°), partially resolved methoxyl peaks at δ 3.47, 3.50, 3.65, 3.69, 3.71, 3.75, 3.77, 3.88, *t*-H_α 2.67 (keto), *t*-H_β 4.59 (enol) and 4.70 (keto), enolic hydroxyl 12.52. The relative peak intensities and positions varied considerably with solvent, temperature, and concentration.

Anal. Calcd for $C_{24}H_{26}O_{17}$: C, 49.15; H, 4.47. Found: C, 49.15; H, 4.69.

Tetramethyl 2-[1-Deuterio-3-oxo-1,2,3-tris(methoxycarbonyl)-propyl]-1-methoxy-7-oxabicyclo[2.2.1]hepta-2,5-diene-3,4,5,6-tetracarboxylate (8b).—A solution of 5 g of **1a** in 100 ml of dioxane was treated with 100 ml of deuterium oxide. The reaction was considerably slower than with water. After 30 days, little or no **1a** could be detected by thin layer chromatography (see above). Solvent was removed under reduced pressure, and the oily residue was twice crystallized from acetone–hexane and once from methanol, giving white crystalline **8b**, mp 143–144.4°. The nmr spectrum was the same as that of **8a** except that the two peaks assigned to the *t*-β-hydrogens at δ 4.59 and 4.70 ppm were absent.

Anal. Calcd for $C_{24}H_{25}DO_{17}$: C, 49.07, H + D = 4.63; excess atom % D, 3.85. Found: C, 49.27; H + D = 4.63; excess atom % D, 3.82.

Reaction of 5 with Hydrogen Bromide. Trimethyl 5-[2-Bromo-1,2,3-tris(methoxycarbonyl)cyclopropyl]-3,6-dihydroxytrimellitate (6).—A solution of 24.1 g of **5** in 500 ml of benzene was treated with excess hydrogen bromide at room temperature. The solution was allowed to stand overnight at room temperature, and part of the solvent and excess hydrogen bromide were removed on a rotary evaporator under reduced pressure. The resulting solution was diluted with dichloromethane, dried ($MgSO_4$), and concentrated. The residual viscous, yellow oil was crystallized from *ca.* 75 ml of methanol giving light yellow **6** (10.7 g 46%): mp 196.2–197.5 (from the filtrate, 4.0 g of **3a** was isolated); $\lambda_{\max}$ 375 mμ (ϵ 6520), 266 (6640), 225 sh (15,100); nmr (acetone-d_6) δ 3.00 [1], 3.67 [3], 3.80 [3], 3.85 [3], 3.90 [3], 3.95 [3], 4.01 [3]; $\nu_{\max}$ 3420 (m), 3020 (w), 2920 (m), 1750 (vs), 1685 (s), 1575 (w), 1500 cm^{-1} (w).

Anal. Calcd for $C_{21}H_{21}O_{14}Br$: C, 43.69; H, 3.67; Br, 13.84. Found: C, 43.83; H, 3.71; Br, 13.94.

This compound was also obtained in nearly quantitative yield by treatment of **7** in benzene with hydrogen bromide.

Dimethyl Ether of 6. Methyl Ether of 3a. Trimethyl 5-[2-Bromo-1,2,3-tris(methoxycarbonyl)cyclopropyl]-3,6-dimethoxytrimellitate (4).—A solution of 15 g (0.025 mol) of **3a** in 30 ml

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(18) The following method of recrystallization from methanol was found to be superior to the conventional one. No heating is required. The compound to be recrystallized was dissolved in chloroform or dichloromethane. Solvent was then removed under reduced pressure on a rotary evaporator, avoiding the introduction of seed crystals. The resulting oily residue was dissolved in a small amount of warm methanol, decolorizing charcoal was added, and the solution was filtered rapidly through a pressure funnel into a clean flask. The filtrate was seeded if necessary to induce crystallization.

(19) We wish to thank Professor R. J. Crawford at the University of Alberta for this spectral measurement.

of dichloromethane was treated with 0.028 mol of diazomethane in ethanol–ether at 0°. Excess diazomethane was destroyed with acetic acid, and the solution was concentrated and crystallized from 50 ml of methanol to give 12.7 g (two crops) of **4**, mp 127–128.4°,[18] $\lambda_{\max}^{\mathrm{EtOH}}$ 302 mμ (ε 4510).

Anal. Calcd for $C_{23}H_{25}O_{14}Br$: C, 45.63; H, 4.16. Found: C, 45.93; H, 4.12.

This compound was also obtained in high yield by treatment of **6** with 2 equiv of diazomethane.

Adduct of 1a with Triphenylphosphine (11).—A solution of 1.14 g of **1a** in 300 ml of ether was treated with a solution of 0.53 g of triphenylphosphine in 20 ml of ether. The deep red solution was filtered. It slowly deposited 1.62 g (97%) of **11**. Larger quantities of **11** were prepared by mixing a solution of 20 g of **1a** in 100 ml of benzene with 18 g (excess) of triphenylphosphine in 50 ml of benzene. The red solution was added dropwise while stirring to 1.6 l. of pentane. The bright orange-red crystals (29 g, 99%) were washed with pentane.

A portion recrystallized from dichloromethane–carbon tetrachloride formed deep-red crystals: mp 213–214°; $\lambda_{\max}^{\mathrm{EtOH}}$ 468 mμ (ε 10,300); $\nu_{\max}$ 3080 (w), 3020 (w), 2970 (m), 2960 (w), 1730 (vs), 1635 (ms), 1490 (m), 1440 (vs), 1320 (b,s), 1260 (b, vs), 1200 (s), 1140 (s), 1107 (s), 1075 (m), 1035 (b, m), 975 (w), 915 (w), 860 (w), 815 (w), 780 (b,m), 760 (m), 715 (m), 693 cm^{-1} (m).

Anal. Calcd for $C_{42}H_{39}O_{16}P$: C, 60.72; H, 4.74; P, 3.73. Found: C, 60.35; H, 5.02; P, 3.67.

Photoisomer of 1a. Octamethyl Semibullvaleneoctacarboxylate (13).—A solution of 2.5 g of **1a** in 700 ml of ether was photolyzed for 8 hr in a water-cooled, quartz flask using a Rayonet photochemical reactor with 16 G-8-T5 germicidal lamps.

Solvent was removed under reduced pressure, and the residue was crystallized from methanol to give **13** (white crystals): mp 162–163.2°; $\lambda_{\max}$ 225 mμ (ε 12,400); $\lambda_{\min}$ 205 mμ (ε 11,000) (lit.[3] $\lambda_{\max}$ 222 mμ, ε 12,300); $\nu_{\max}$ 3020 (w), 2960 (mw), 2860 (w), 1755–1742 (vs), 1626 (m), 1460 (s), 1335 (s), 1280 (b, vs), 1210 (s), 1175 (s), 1093 (m), 1058 (m), 1025 (m), 990 (b,m), 918 (w), 890 (w), 853 (mw), 846 (m), 813 (m), 774 (w), 744 (m), 667 cm^{-1} (w); nmr (acetone-d_6) δ 3.78 [6], 3.76 [12], 3.72 [6] (integration checked at 100 Mc; no change in the spectrum occurred on cooling to −90°); nmr (chloroform-*d*) τ 6.21 [18], 6.26 [6] (a shoulder appears on the low-field side of the τ 6.21 peak) (lit.[3] τ 6.21 [18], 6.26 [6]).

Anal. Calcd for $C_{24}H_{24}O_{16}$: C, 50.71; H, 4.26. Found: C, 50.91; H, 4.33.

Reaction of Dimethyl Acetylenedicarboxylate with Hydroquinone. Dimethyl 2-(4-Hydroxyphenyloxy)but-2-ene-1,4-dioate (17).—A mixture of 100 g of dimethyl acetylenedicarboxylate and 100 g of hydroquinone was stirred in an oil bath at 100° under nitrogen for 3 days. The product was dissolved in ether and extracted with excess 10% aqueous sodium carbonate solution. The ether layer was washed with citric acid solution and dried ($MgSO_4$). On distillation under reduced pressure (oil-bath temperature = 100°) 67 g of dimethyl acetylenedicarboxylate was recovered. The residue crystallized slowly giving 5.0 g of crude **17**. Recrystallization from benzene gave 4.25 g of yellow crystals: mp 105–106.2°; $\lambda_{\max}$ 226 mμ (ε 16,900), 284 (3100), 320 sh (ε 1690); nmr (chloroform-*d*) δ 8.08 [1], 6.81 [4], 6.43 [1], 3.71 [3], 3.68 ppm [3].

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.29; H, 4.85.

Pyrolysis of 7. Isolation of Dimethyl Oxalacetate and the Dimer of Dimethyl 3-[1,2,3-Tris(methoxycarbonyl)-2-cyclopropen-1-yl]-2-methoxyfuran-4,5-dicarboxylate (10b).—A 15 mm × 200 mm tube jacketed at its upper end with a watercooled condenser was charged with 2.00 g of **7** and about ten 6-mm glass beads. It was evacuated to 0.3-μ pressure and heated at its lower end to 140°. The solid white **7** melted and vigorously evolved a vapor which condensed as large colorless crystals in the cooled portion of the tube. Heating was continued for 5 hr. The tube was cooled and inverted, and the crystalline sublimate was washed out with acetone. Solvent was removed under reduced pressure, and the white solid residue was recrystallized from hexane to obtain 0.34 g (62%) of dimethyl oxalacetate, mp 72–74°, whose infrared spectrum was identical with that of a sample of the authentic material, mp 71.5–73°, prepared by the method of Fenton and Jones.[20]

The nonvolatile residue in the tube (1.64 g) was crystallized from methanol to yield 0.83 g (57%) of light-yellow crystals of **10b**: mp *ca.* 190° dec; $\lambda_{\max}$ 300 mμ (ε 10,400); nmr (chloroform-*d*) 3.29 [3], 3.59 [3], 3.60 [3], 3.67 [3], 3.71 [3], 3.75 [6], 3.78 [3], 3.87 [3], 3.90 [3], 3.96 [3], 3.99 [3]; $\nu_{\max}$ 3660 (w), 3430 (w), 3030 (m), 2960 (m), 1883 (m), 1745 (vs), 1635 (m), 1580 cm^{-1} (ms).

Anal. Calcd for $C_{38}H_{36}O_{24}$: C, 50.71; H, 4.26; mol wt, 853. Found: C, 50.31; H, 4.44; mol wt, 829 (vapor pressure osmometry, 37% in CH_2Cl_2).

Trapping of 10a by Pyrolysis of 7 in the Presence of Dimethyl Acetylenedicarboxylate. Synthesis of 1a.—A mixture of 0.20 g of **7**, 0.5 g of dimethyl acetylenedicarboxylate, and 6.7 mg of hydroquinone in a sealed tube was heated to 140° for 1 hr. The oily product was cooled and seeded with **1a**. After 3 days, the crystalline mass was slurried with 3 ml of ether, cooled to 5°, allowed to stand overnight, and filtered. The crystals after washing with ether weighed 0.138 g (71%). The infrared spectrum was identical with that of **1a** as described above. After recrystallization from ether–pentane, the white crystals melted at 103.6–104.7°.

In the control experiment, 0.7 g of dimethyl acetylenedicarboxylate and 8.1 mg of hydroquinone were heated to 140° for 1 hr. On seeding with **1a**, no crystals deposited. The infrared spectrum of the oily product (1880 cm^{-1}) indicated that little or no **1a** was present.

Trapping of 10a by Pyrolysis of 7 in the Presence of Dimethyl Acetylenedicarboxylate-d_6. Synthesis of 1c.—A mixture of 0.30 g of **7**, 0.47 g of dimethyl acetylenedicarboxylate-d_6, and 10 mg of hydroquinone was sealed in a glass tube under nitrogen, heated to 140° for 1 hr, cooled, and seeded with a small crystal of **1a**. Work-up as in the preceding section gave 0.196 g of **1c** in two crops and 0.25 g of unreacted dimethyl acetylenedicarboxylate-d_6. After recrystallization from ether–pentane the white needles of **1c** melted at 106.5–107.2°: $\nu_{\max}$ 2960 (w), 2255 (w), 2180 (mw), 2120 (w), 2080 (mw), 1880 (m), 1725 (vs), 1625 cm^{-1} (m); nmr (acetone-d_6) δ 3.584 [3], 3.642 [3], 3.707 [3], 3.839 [3], 3.848 [3], 3.920 [3].

Anal. Calcd for $C_{24}H_{18}D_6O_{16}$: C, 50.18; H + D, 5.26; excess atom % D, 25.0. Found: C, 50.44; H + D, 5.44; excess atom % D, 24.95.

Dimethyl Acetylenedicarboxylate-d_6.—Methanol-d_4 (5 g) (Merck Sharp and Dohme of Canada, Ltd.) was placed in an ice-cooled 50-ml flask, and 2.2 ml of sulfuric acid was added cautiously. To the cold solution, 2.0 g of the potassium acid salt of acetylenedicarboxylic acid was added. The flask was stoppered, and the mixture was stirred for 12 days at room temperature. The mixture was filtered, and the more volatile portion of the filtrate was distilled in a vacuum line at room temperature in order to recover unreacted deuteriomethanol (1.9 g). The residue was stirred with ice and dichloromethane. The solid material from the filtration was stirred with ice water and dichloromethane. The dichloromethane extracts were combined and washed with water, dilute aqueous potassium bicarbonate, and water, then dried ($CaCl_2$), concentrated, and distilled to yield 1.1 g of dimethyl acetylenedicarboxylate-d_6: bp 51–52° (3.2 mm); $n^{25}D$ 1.4427; mp 0.0–0.3°; $\nu_{\max}$ 3440 (w), 2270 (m), 2200 (m), 2130 (w), 2080 (m), 1730 (vs), 1490 (w), 1290 (b, vs), 1088 (s), 970 (ms), 934 (w), 901 (m), 883 (m), cm^{-1} (ms).

Anal. Calcd for $C_6D_6O_4$: C, 48.64; D, 8.16. Found: C, 48.60; D, 7.99.

Registry No.—**1a,** 16199-47-6; **1b,** 16214-86-1; **1c,** 16291-02-4; **2,** 5202-32-4; **3a,** 16199-08-9; **3b,** 16199-21-6; **4,** 16199-09-0; **5,** 16199-10-3; **6,** 16199-11-4; **8a,** 16199-12-5; **8b,** 16199-13-6; **10b,** 16199-22-7; **11,** 16240-69-0; **13,** 16286-16-1; **17,** 16199-23-8; dimethyl acetylenedicarboxylate-d_6, 16199-24-9.

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