form-hexane, mp 214-217 °C (lit.[17] mp 217 °C from ethanol), was obtained in 47% yield: IR (Nujol) 1785 (vs), 1765 (m), 1745 (w), (C=O), 1650 (C=N); NMR (TFA) δ 4.06 (s, 3 H, OCH_3), 7.23 (d, J = 10 Hz, 2 H), 7.39-7.90 (m, 6 H, vinyl H and C_6H_5), 8.33 (d, J = 10 Hz, 2 H).

Oxidation of 1 with SeO_2. A mixture of 1.0 g (3.72 mmol) of 1 in 25 mL of acetic anhydride containing 1 drop of pyridine and 0.67 g (6 mmol) of SeO_2 was refluxed for 18.5 h. After cooling, the mixture was diluted with ether to precipitate selenium, which was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in ether (300 mL) and washed three times with H_2O and then with saturated $NaHCO_3$ solution (until the washes were basic). The ether solution was dried (Na_2SO_4), filtered, and concentrated in vacuo, leaving a solid residue which was dissolved in hot isopropyl alcohol, yielding 0.51 g (55%) of 3, mp 163-166 °C.

Oxidation of 2 with Phenylselenyl Chloride/H_2O_2. To a solution of 0.77 g (3.55 mmol) of 2 in 40 mL of ethyl acetate was added 0.77 g (4 mmol) of PhSeCl. The solution was stirred 8 h at room temperature followed by 6 h at reflux. Triethylamine (0.49 mL, 3.55 mmol) was added, and 30 min later TEA·HCl (0.31 g, 60%) was filtered. To the filtrate was added 0.7 mL (8.0 mmol) of 30% H_2O_2, and this solution stirred at room temperature for 4 h. At the end of this time the solution was washed with two 25-mL portions of water and once with saturated Na_2CO_3 solution. The organic layer was separated, dried (Na_2SO_4), filtered, and concentrated in vacuo, leaving a yellow solid residue. Crystallization from isopropyl alcohol gave 157 mg (21%) of crystalline 3, mp 165-167 °C.

Oxidation of 2 with *t*-BuOCl in the Presence of K_2CO_3. A mixture of 0.62 g (2.48 mmol) of 2, 0.4 mL (3.36 mmol) of *t*-BuOCl, and 2.0 g (14.5 mmol) of finely divided anhydrous K_2CO_3 in 60 mL of CCl_4 was stirred at room temperature for 16 h and then refluxed 6.5 h. The reaction mixture was filtered and concentrated to dryness in vacuo, leaving a yellow solid residue. A yield of 0.4 g (66%) of 3, mp 161-164 °C, was obtained by crystallization from isopropyl alcohol.

Oxidation of 2 with DDQ. To a dry three-necked flask was added 0.269 g (1.00 mmol) of 1, 0.206 g (1.00 mmol) of DCC, and 5 mL of dioxane under nitrogen. The mixture was stirred for 1 h at room temperature, the DCU was filtered by positive nitrogen pressure, and the filtrate was transferred to a flask containing 0.381 mL (3.00 mmol) of TMCS, 0.836 mL (6.00 mmol) of triethylamine, and 5 mL of dioxane under nitrogen. The mixture was stirred for 1 h and transferred to a flask containing 0.227 g (1.00 mmol) of DDQ and 0.124 mL (0.50 mmol) of disilylacetamide in 5 mL of dioxane under nitrogen. The reaction mixture was stirred 1 h and evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed twice with saturated $NaHSO_3$, twice with saturated $NaHCO_3$, and once with saturated NaCl. The solution was dried ($MgSO_4$), filtered, and evaporated under reduced pressure to yield a yellow solid which was crystallized from 2-propanol to yield 187 mg (75%) of 3.

Oxidation of 2 with Palladium(II) Acetate. In a dry three-necked flask, 1.00 mmol of 1 was converted into 2 as before, and the filtrate was transferred into a flask containing 0.381 mL (3.00 mmol) of TMCS, 0.836 mL (6.00 mmol) of TEA, and 5 mL of dioxane under nitrogen. The mixture was stirred for 1 h, filtered by positive nitrogen pressure, and evaporated under reduced pressure to give a light yellow oil which was taken up in 3 mL of CH_3CN and transferred into a flask containing 0.225 g (1.00 mmol) of $Pd(OAc)_2$ in 3 mL of CH_3CN under nitrogen. The reaction mixture was stirred for 40 h at room temperature. Quantitative liquid chromatography detected 3 present in 24% yield. Filtration of the reaction mixture, followed by evaporation at reduced pressure, yielded a crude yellow solid which was purified on a 3 × 15 cm silica gel column by using 4% EtOAc in petroleum ether as the eluant. Fractions containing 3 were combined and evaporated under reduced pressure to give 39 mg (16% yield) of 3.

Oxidation of 4 with DDQ. To 0.269 g (1.00 mmol) of benzoylphenylalanine in 5 mL of dioxane was added 0.206 g (1.00 mmol) of DCC. The reaction was stirred for 1 h. The DCU was filtered and the filtrate transferred to a flask containing 0.227 g (1.00 mmol) of DDQ and 0.132 mL (1.00 mmol) of collidine in 1 mL of dioxane. The reaction was stirred for 24 h and yielded 30% of 3 by quantitative high-pressure LC.

Oxidation of 4 with Palladium Acetate. To 1.00 mmol of benzoylphenylalanine in 5 mL of dioxane was added 1.00 mmol of DCC. The reaction was stirred for 1 h and the DCU filtered. The dioxane was evaporated under reduced pressure to give an oil which was dissolved in 5 mL of acetonitrile and added to a flask containing 1.00 mmol of palladium(II) acetate in 1 mL of acetonitrile. The reaction was stirred for 24 h and yielded 23% of 3 by quantitative high-pressure LC.

Registry No. 1, 2566-22-5; 2, 21453-79-2; 3, 842-74-0; 4, 72659-38-2; 2-(*p*-nitrophenyl)-4-benzylidene-2-oxazolin-5-one, 15601-50-0; 2-(*p*-methoxyphenyl)-4-benzylidene-2-oxazolin-5-one, 34108-13-9; *N*-(*p*-nitrobenzoyl)phenylalanine, 24758-96-1; *N*-(*p*-methoxybenzoyl)phenylalanine, 59490-31-2.

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Preparation of Muconic Acid Anhydrides. Characterization of the 1-Oxacyclohepta-3,5-diene-2,7-dione Structure

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Several muconic acid anhydrides have been prepared from the corresponding *o*-benzoquinones by oxidation with monoperphthalic acid.[1-3] These species are synthetically useful intermediates for the formation of muconic acid derivatives by a simple hydrolytic ring opening.[2] There is a lack of information on the isolation and characterization of these cyclic anhydrides, presumably because of their tendency to undergo this facile ring cleavage to the open-chain systems. During our studies on the proposed new route to caprolactam involving the copper(II)-induced oxidation of phenol,[4,5] we uncovered carbon-carbon bond cleavage reactions that may proceed via muconic acid anhydride intermediates. In order to test this possibility we required pure samples of the substituted 1-oxacyclohepta-3,5-diene-2,7-dione derivatives 2, 4, and 6. In this report we describe a general method for preparation and isolation of these anhydrides and briefly discuss their structural features and several typical chemical transformations.

Results and Discussion

The required anhydrides were prepared simply by addition of a slight molar excess (10%) of *m*-chloroperbenzoic acid to a solution of the corresponding *o*-benzoquinones in dry methylene chloride at 0 °C. The oxidations were completed in 5-10 min as indicated by the initial deep-red clear solution turning to a heterogeneous light-yellow mixture. The majority of the generated *m*-chlorobenzoic

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(3) F. R. Hewgill and S. L. Lee, *J. Chem. Soc. C.*, 2080 (1969).
(4) (a) M. M. Rogić and T. R. Demmin, *J. Am. Chem. Soc.*, 100, 5472 (1978). (b) M. M. Rogić and T. R. Demmin, "Aspects of Mechanism and Organometallic Chemistry", J. H. Brewster, Ed., Plenum Press, New York, NY, 1978, p 141.
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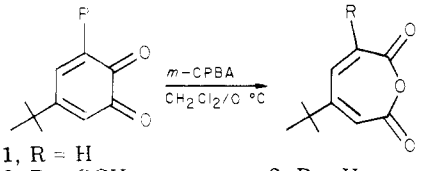
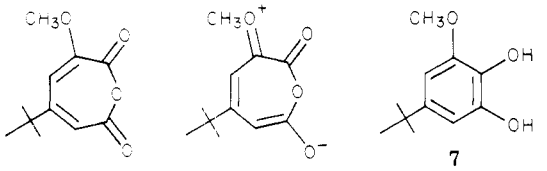


1, R = H
3, R = OCH_3
5, R = $C(CH_3)_3$

2, R = H
4, R = OCH_3
6, R = $C(CH_3)_3$

acid was then removed by filtration at −78 °C. The resulting cold solutions, containing 10–15 mol % of *m*-chlorobenzoic acid as the only NMR-detectable impurity, were evaporated to dryness at 0 °C, and the crude anhydrides were purified by chromatography.[6] Once purified, the anhydrides appear stable at 0 °C when protected from moisture.

The NMR spectra properties listed in Tables I and II are consistent with the proposed substituted 1-oxacyclohepta-3,5-diene-2,7-dione structures. A noteworthy feature in the ^1H NMR of the methoxy-substituted anhydride **4** is the unusually large long-range coupling between the methoxy group and the C_4 proton which was verified by decoupling experiments. This phenomenon may reflect

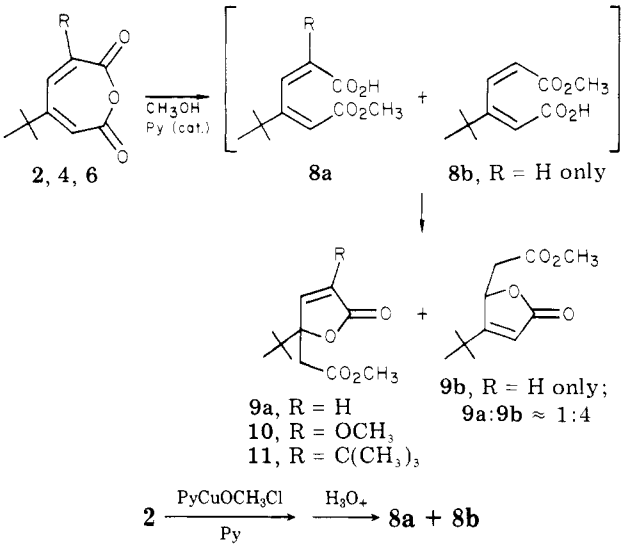


4 4a 7

a substantial contribution from resonance structure **4a** to the overall electronic description of the molecule. With the increased double bond character at the methoxy oxygen, homoallylic type coupling may be effectively transmitted. Long-range coupling, ~0.4 Hz, is also present in the analogous *o*-benzoquinone **3** where similar resonance may exist. However, in the related 3-methoxy-5-*tert*-butylcatechol (**7**), with no resonance possible as in **3** and **4**, long-range coupling between the methoxy group and the C_4 proton is completely absent. Further indication that the methoxy group substantially increases electron density in the ring comes from the dramatic upfield shifts of C_4 protons and of the C_4 and C_6 absorptions in the ^1H NMR and ^{13}C NMR spectra (Tables I and II).

Ring Opening by Methanol. Chemical support for the anhydride structural assignment is obtained by the pyridine-catalyzed methanolysis to the muconic acid monomethyl esters **8**[4,5] which were characterized as the α,β-unsaturated γ-lactones **9**,[4,5] **10**, and **11**. The lack of regioselectivity in the nucleophilic attack of methanol (or methoxide) on **2** is not surprising since the *tert*-butyl group should have little steric or electronic influence on the electrophilicity of either carbonyl. Experimentally, the more distant carbonyl is found to be slightly more susceptible to nucleophilic attack. However, with a substituent adjacent to this carbonyl as in **4** and **6**, attack is directed to the other carbonyl, yielding the single products **10** and **11**, respectively.

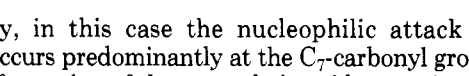
Ring Opening by $(PyCuOCH_3Cl)_2$. The anhydride **2** is also effectively cleaved by the same copper(II) salt, pyridine cupric methoxychloride,[7] employed in the oxidative cleavage of *o*-benzoquinone, catechol, and phenol.[4,5]



2, 4, 6 8a 8b, R = H only

9a, R = H
10, R = OCH_3
11, R = $C(CH_3)_3$

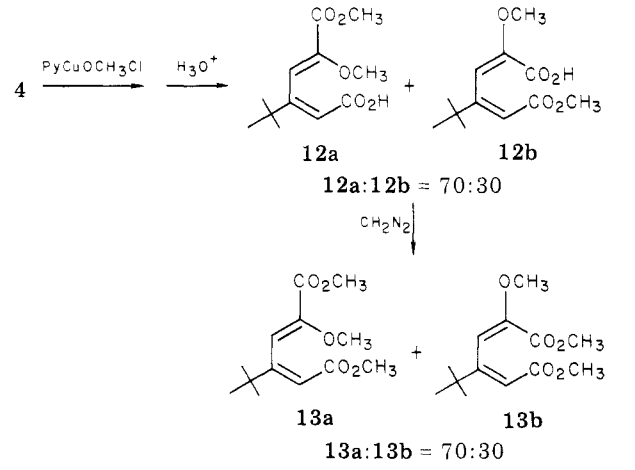
9b, R = H only;
9a:9b ≈ 1:4



2 → **8a + 8b**

Interestingly, in this case the nucleophilic attack by methoxide occurs predominantly at the C_7-carbonyl group, resulting in formation of the open-chain acid esters **8a** and **8b** in a 64:36 ratio.

In the case of the methoxy-substituted anhydride **4**, the ring opening by pyridine cupric methoxychloride afforded, after hydrolysis, a 70:30 mixture of two stable muconic acid monomethyl esters with the stereochemistry tentatively defined as in **12a** and **12b**. The overall chemical structures



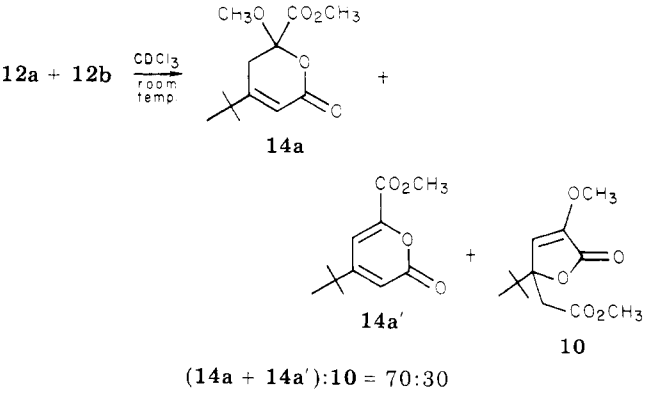
12a 12b

12a:12b = 70:30

13a 13b

13a:13b = 70:30

and isomeric relationship of the half-esters were easily discerned from their ^1H and ^{13}C NMR spectral data, but unequivocal *stereochemical* assignments were impossible. Esterification of the crude product mixture gave a 70:30 mixture of two isomeric diesters **13a** and **13b**, whereas a chloroform solution of **12a** and **12b** indicated slow lactonization to a mixture of 2-pyrones **14a** + **14a′** and γ-lactone **10** in the same 70:30 ratio.[8]



14a

14a′ 10

(14a + 14a′):10 = 70:30

(6) Sephadex LH/20 is the preferred column packing with acetone or tetrahydrofuran as the eluting solvent. Alumina or silica gel are undesirable since the anhydrides undergo ring opening during attempted purification.

(7) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, 31, 549 (1966).

Table I. ^{1}H NMR of 3-Substituted 5-*tert*-Butyl-1-oxacyclohepta-3,5-diene-2,7-diones[a]

compound	R (at C-3)	H-4	H-6	$C(CH_3)_3$
2[b]	6.46 (dd, 12.5 Hz, 0.8 Hz)	6.93 (dd, 12.5 Hz, 2.0 Hz)	6.36 (dd, 2.0 Hz, 0.8 Hz)	1.21
4[b]	3.87 (d, 0.6 Hz)	6.02 (dq,[c] 1.5 Hz, 0.6 Hz)	6.20 (d, 1.5 Hz)	1.23
6[d]	1.15 (s)[c]	6.42 (d, 1.6 Hz)	6.12 (d, 1.6 Hz)	1.27[e]

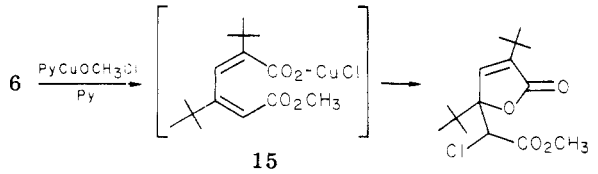
[a] Spectra run in $CDCl_3$ containing 1% Me_4Si, and chemical shifts are reported in δ units. [b] 100 MHz. [c] Distorted. [d] 60 MHz. [e] Assignment may be reversed.

Table II. ^{13}C NMR of 3-Substituted 5-*tert*-Butyl-1-oxacyclohepta-3,5-diene-2,7-diones[a]

compound	C-2/C-7[b]	C-3	C-4	C-5	C-6	other
2	156.86/159.88	119.74	136.54	158.93	124.89	
4	156.76/159.35	150.73	105.87	157.08	112.78	56.40 (MeO)
6	162.04/160.43	159.23	124.21	148.43	115.69	

[a] Spectrum on Varian CFT-20 in $CDCl_3$ containing Me_4Si, with chemical shifts reported in ppm from Me_4Si; *tert*-butyl groups omitted. [b] Assignments may be reversed.

3,5-Di-*tert*-butylmuconic acid anhydride (**6**) is also cleaved by pyridine cupric methoxychloride, apparently to a single intermediate **15** which then cyclizes and is halogenated by excess pyridine cupric methoxychloride to the α-chloro ester lactone **16**. This chlorinated lactone



16 $\xrightarrow[HOAc]{Zn}$ 11

consists of an ~2:1 mixture of diastereoisomers which were separated by careful preparative TLC and fully characterized. Reduction of **16** with Zn/HOAc produced **11** in high yield, thus confirming the integrity of the γ-lactone ring system in the α-chloro ester.

Conclusion

The oxidation of various substituted *o*-benzoquinones by *m*-chloroperbenzoic acid in dry methylene chloride at 0 °C appears to be a simple and efficient procedure for the synthesis and isolation of the substituted muconic acid anhydrides. The anhydrides undergo ring-opening reactions to provide γ-lactone esters or open-chain muconic acid derivatives.

Experimental Section

General Procedures. All melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian T60-A or a HA-100 spectrometer, and ^{13}C NMR spectra were measured on a Varian CFT-20 instrument. Mass spectra were obtained on a Finnigan 3100D chemical ionization mass spectrometer.

3,5-Di-*tert*-butyl-*o*-benzoquinone is commercially available. 4-*tert*-Butyl-*o*-benzoquinone was prepared by the oxidation[9] of the commercially available 4-*tert*-butylcatechol. 5-*tert*-Butyl-3-methoxy-*o*-benzoquinone was similarly prepared by oxidizing[9] the corresponding catechol, which in turn was obtained by the *tert*-butylation[10] of 3-methoxycatechol.

General Procedure for the Oxidation of *o*-Benzoquinones. 5-*tert*-Butyl-1-oxacyclohepta-3,5-diene-2,7-dione (2). A solution of 4-*tert*-butyl-*o*-benzoquinone (1.64 g, 10 mol) in 30 mL of dry methylene chloride was cooled to 0 °C under a nitrogen atmosphere. Then solid *m*-chloroperbenzoic acid (2.24 g of 85% technical grade material, ~11 mol) was added in portions over 1 min. The initially deep-red clear solution turned to a heterogeneous light-yellow mixture usually after ca. 5 min. Most of the generated *m*-chlorobenzoic acid was then removed by filtration at −78 °C. Evaporation of the solution at 0 °C gave the crude anhydride containing 10–15 mol % of *m*-chlorobenzoic acid as the only impurity detected by NMR analysis. Purification by chromatography over Sephadex LH/20 using acetone as eluent gave 1.15 g (64% yield) of 5-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (**2**) as a white solid; recrystallization from hexane gave colorless plates: mp 76–78 °C; IR (CCl_4) 1775, 1740 cm^{-1}; UV (cyclohexane) λ_{max} 260 nm (ϵ 3940); mass spectrum (CI (methane)) MH^+ at *m/e* 181. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.62; H, 6.93.

The following muconic acid anhydrides were prepared and isolated in a similar manner.

5-*tert*-Butyl-3-methoxy-1-oxacyclohepta-3,5-diene-2,7-dione (4): ca. 90% crude yield, 52% yield as light pink rhomboid crystals after chromatography and recrystallization from ether (−30 °C); mp 57.5–59.5 °C; IR (CCl_4) 2840, 1787, 1743 cm^{-1}; UV (cyclohexane) λ_{max} 288 nm (ϵ 2340), 267 and 257 (shoulders); mass spectrum (CI (methane)) MH^+ at *m/e* 211. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 63.01; H, 6.79.

3,5-Di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (6): 66% yield as large colorless cubes after chromatography and recrystallization from pentane; mp 93–94 °C; IR (Nujol) 1785, 1745 cm^{-1}; UV (cyclohexane) λ_{max} 247.5 nm (ϵ 1723); mass spectrum (CI (methane)) MH^+ at *m/e* 237. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.25; H, 8.69.

Methanolysis of Anhydride 2. A solution of the anhydride **2** (0.18 g, 1 mmol) in dry methylene chloride (1 mL) was added via syringe over 10 min to a solution of dry pyridine (1 mL) in dry methanol (10 mL) at room temperature with magnetic stirring under a nitrogen atmosphere. After the solution was stirred for 2 h, it was evaporated at room temperature to yield 0.21 g (100% yield) of yellow oil identified by NMR as a mixture of lactones **9a** and **9b** in a ratio of **9a**:**9b** = 1:4. An additional unidentified methoxy (δ 3.60) and *tert*-butyl (δ 1.13) absorption amounting to less than 10% of the total was also detected.

Methanolysis of Anhydride 4. A crude sample of anhydride **4**, prepared by the *m*-CPBA oxidation of *o*-quinone **3** (1.00 g, 5.15 mmol) in 15 mL of methylene chloride, was treated with dry methanol (10 mL) and pyridine (0.5 mL) at 0 °C and then warmed to room temperature for 18 h. NMR analysis indicated ca. 80–85% of lactone ester **10** and 15–20% of a mixture of four other components, including unreacted anhydride **4**. The reaction mixture was evaporated and triturated with pentane (75 mL), and **10** was filtered off in 59% yield as a white solid, mp 66–73 °C. Recrystallization from hexane/methylene chloride gave colorless branches: mp 78–79 °C; IR (Nujol) 3130, 1770, 1750, 1663 cm^{-1}; mass spectrum (CI (methane)) MH^+ at *m/e* 243; NMR ($CDCl_3$) δ 6.12 (s, —CH=, 1), 3.77 (s, OCH_3, 3), 3.58 (s, CO_2CH_3, 3), 2.88

(8) This establishes that the carbomethoxy group in the minor half-ester is located on the carbon–carbon double bond bearing the *tert*-butyl group. By making the reasonable assumption that in all isomers the carbomethoxy or carboxyl group is trans to its neighboring (adjoining) *tert*-butyl group, it follows that in the two half-esters **12a** and **12b** the methoxy group and the vicinal hydrogen must be trans in one isomer and cis in the other.

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(10) F. E. Stockelbach, U.S. Patent 2 137 815, 1939.

(br, CH_2CO_2, 2), 0.99 (s, $(CH_3)_3C$, 9); ^{13}C NMR ($CDCl_3$) δ 169.71 (s, CO_2CH_3), 166.88 (s, CO_2), 147.68 (s, =C(OCH$_3$)—), 116.68 (d, —CH=), 88.16 (s, CH_2C), 58.12 (q, =C(OCH$_3$)—), 51.75 (q, CO_2CH_3), 38.46 (t, CH_2CO_2), 38.04 (s, $C(CH_3)_3$), 25.18 (q, $C(CH_3)_3$). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.68; H, 7.78.

Methanolysis of Anhydride 6. A solution of anhydride **6** (0.10 g, 0.42 mmol) in dry methanol (10 mL) was treated with 0.5 mL of pyridine and stirred at room temperature under nitrogen for 18 h. Evaporation provided 0.11 g (98% yield) of lactone ester **11** as a white solid: mp 68–69 °C; IR (Nujol) 1750, 1735 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 269; NMR ($CDCl_3$) δ 6.95 (s, CH=, 1), 3.57 (s, CH_3O, 3), 2.87 (ABq, CH_2CO_2, 2), 1.23 (s, $C(CH_3)_3$, 9), 0.98 (s, $C(CH_3)_3$, 9); ^{13}C NMR ($CDCl_3$) δ 171.09 (s, CO_2), 169.71 (s, CO_2CH_3), 146.06 (s, =CC(CH$_3$)$_3$), 143.68 (d, CH=), 88.47 (s, =CHC), 51.74 (q, CH_3O), 38.04 (t, CH_2CO_2), 37.79 (s, $(CH_3)_3CCCH_2$), 31.55 (s, $(CH_3)_3CC$=), 28.09 (q, $(CH_3)_3CC$=), 25.37 (q, $(CH_3)_3CCCH_2$). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 67.57; H, 8.75.

Reaction of Anhydride 2 with $(PyCuOCH_3Cl)_2$. A solution of the anhydride **2** (0.18 g, 1 mmol) in methylene chloride (1 mL) was added via a pump-driven syringe over 20 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (0.63 g, 3 mmol) in pyridine (30 mL) at room temperature under a nitrogen atmosphere. After an additional 50 min the mixture was evaporated in vacuo and hydrolyzed by dissolving in methylene chloride (100 mL), cooling in an ice bath, and slowly adding 100 mL of 2 N hydrochloric acid with vigorous stirring. The organic layer was dried over $MgSO_4$ and evaporated to give 0.18 g of a colorless oil. NMR analysis revealed a mixture of acid esters **8a** and **8b** in a 64:36 ratio.

Reaction of Anhydride 4 with $(PyCuOCH_3Cl)_2$. The anhydride **4** was prepared as described above from 3-methoxy-5-*tert*-butyl-*o*-benzoquinone (**3**) (1.00 g, 5.15 mmol) and used immediately without further purification. Crude **4**, dissolved in 5 mL of methylene chloride, was added via syringe over 10 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (6.40 g, 30.6 mmol) in dry pyridine (310 mL) under a nitrogen atmosphere at 0 °C. After stirring 30 min at 0 °C and 75 min at room temperature the solution was evaporated in vacuo, and the residue was extracted with 300 mL of ether. The green copper(II) salts were filtered off and acid hydrolyzed as before. Evaporation of the organic layer gave 1.00 g of amber oil shown by NMR to be ~15% *m*-CPBA and ~85% of a 70:30 mixture of acid esters **12a** and **12b**.

Stirring with pentane (30 mL) at room temperature effected purification and precipitation of **12a** + **12b** (0.75 g, 60% yield): mp 68.5–73 °C; IR (Nujol) 3500–2400, 1760, 1755, 1745, 1725, 1698, 1645, 1280, 1208 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 243. Recrystallization from pentane/methylene chloride gave white clusters (isomer mixture), mp 83–84 °C. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.30; H, 7.42.

Careful fractional crystallization from pentane/methylene chloride gave the less soluble minor isomer, 2-methoxy-4-*tert*-butyl-2(*Z*),4(*Z*)-hexadienedioic acid 6-methyl ester (**12b**): mp 89–92.5 °C; NMR ($CDCl_3$) δ 5.88 (d, J = 2.0 Hz, =CHCO$_2$CH$_3$, 1), 5.79 (br d, $J \approx 2$ Hz, CH=C(OCH$_3$), 1), 3.79 (d, $J \approx 0.5$ Hz, =C(OCH$_3$), 3), 3.66 (s, CO_2CH_3, 3), 1.17 (s, $(CH_3)_3C$, 9); ^{13}C NMR ($CDCl_3$) δ 167.44 (CO_2H), 161.28 (CO_2CH_3), 115.15 (=CHCO$_2$), 108.78 (CH=C(OCH$_3$)), 56.04 (=C(OCH$_3$)-), 51.29 (CO_2CH_3), 38.24 ($C(CH_3)_3$), 29.05 ($C(CH_3)_3$); fully substituted sp^2 carbons C_2 and C_4 were not detected.

The mother liquors were enriched in the major isomer, 2-methoxy-4-*tert*-butyl-2(*E*),4(*Z*)-hexadienedioic acid 1-methyl ester (**12a**): mp 78–86 °C; NMR ($CDCl_3$) δ 5.89 (d, J = 1.9 Hz, =CHCO$_2$H, 1), 5.70 (br d, J = 1.9 Hz, CH=C(OCH$_3$), 1), 3.76 (d, $J \approx 0.5$ Hz, =C(OCH$_3$), 3), 3.73 (s, CO_2CH_3, 3), 1.17 (s, $(CH_3)_3C$); ^{13}C NMR ($CDCl_3$) δ 172.41 (CO_2H), 167.25 (CO_2CH_3), 163.69 (C=CCO$_2$H), 146.18 (=C(OCH$_3$)-), 114.95 (=CCO$_2$H), 107.08 (-C=C(OCH$_3$)-), 55.86 (=C(OCH$_3$)-), 51.97 (CO_2CH_3), 38.25 ($C(CH_3)_3$), 29.07 ($C(CH_3)_3$).

After standing in $CDCl_3$ solution for 28 days at room temperature, a mixture of **12a** and **12b** had rearranged to a mixture comprising **10** (29%), **14a** (58%), and **14a'** (13%).[4] Structure **14a** had the following spectral features: NMR ($CDCl_3$) δ 5.63 (t, J = 1.6 Hz, CH_2C=CHCO$_2$, 1), 3.17 (d, J = 1.6 Hz, CH_2C=CH, 2), 1.08 (s, $(CH_3)_3C$, 9).

Dimethyl 2-Methoxy-4-*tert*-butyl-2,4-hexadienedioate (13). A solution of **12a** and **12b** (4.70 g, 19.4 mmol, 70:30 isomer mixture) in diethyl ether (150 mL) was treated with excess ethereal diazomethane at 0 °C. The mixture was stirred at room temperature overnight, concentrated, and evaporatively distilled to give **13** (4.61 g, 93% yield): bp 112 °C (0.25 mm); IR (CCl_4) 2840, 1735, 1635, 1435, 1240, 1172 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 257; UV (methanol) λ_{max} 212 nm (ϵ 9640), ~270 (3790, poorly resolved); **13a** NMR ($CDCl_3$) δ 6.78 (d, J = 1.4 Hz, CH=C(C-O_2CH_3), 1), 5.94 (d, J = 1.4 Hz, =$CHCO_2$, 1), 3.85 (s, slightly broadened?, =C(OCH$_3$), 3), 3.71 and 3.62 (2s, CO_2CH_3, 2 × 3), 1.15 (s, $(CH_3)_3C$, 9); **13b** NMR ($CDCl_3$) δ 5.90 (d, J = 2.0 Hz, =$CHCO_2$, 1), 5.69 (br d, $J \approx 1.8$–2.0 Hz, CH=C(OCH$_3$), 1), 3.78 (d, $J \approx 0.6$ Hz, CH=C(OCH$_3$), 3), 3.74 and 3.69 (2s, CO_2CH_3, 2 × 3), 1.16 (s, $(CH_3)_3C$, 9). The ^{13}C NMR is consistent with structures **13a** and **13b**. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.37; H, 7.54.

Reaction of Anhydride 6 with $(PyCuOCH_3Cl)_2$. A solution of the anhydride **6** (0.24 g, 1.0 mmol) in dry pyridine (5 mL) was added via pump-driven syringe over 60 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (1.25 g, 6 mmol) in 60 mL of pyridine at room temperature under nitrogen. After 30 min the green solution was evaporated at 25 °C and the resulting green solid was stirred with 200 mL of pentane at room temperature for 1 h. Filtration and evaporation gave 0.25 g of a light yellow oil shown by NMR to be 95% α-chloro ester **16** (as a 60:40 mixture of diastereoisomers) and 5% ester lactone **11**. Analytical samples were obtained by preparative TLC (silica gel/methylene chloride): **16**, R_f 0.84; mp 105–106 °C as colorless cubes from pentane/methylene chloride; IR (neat, prior to crystallization) 3150, 1765, 1650 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 303 (one Cl present); NMR ($CDCl_3$) δ 7.15 (s, CH=, 1), 4.80 (s, CHCl, 1), 3.79 (s, CH_3O, 3), 1.28 and 0.60 (2 s, $(CH_3)_3$, 2 × 9); ^{13}C NMR consistent with structure. Anal. Calcd for $C_{15}H_{23}O_4Cl$: C, 59.50; H, 7.66. Found: C, 59.48; H, 7.38; **16**, R_f 0.70; mp 84–85 °C as needles from pentane at −70 °C; IR (Nujol) 3125, 1760, 1645 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 303 (one Cl present); NMR ($CDCl_3$) δ 7.10 (s, CH=, 1), 4.80 (s, CHCl, 1), 3.68 (s, CH_3O, 3), 1.27 and 1.07 (2s, $(CH_3)_3C$, 2 × 9); ^{13}C NMR consistent with structure **16**. Anal. Calcd for $C_{15}H_{23}O_4Cl$: C, 59.50; H, 7.66. Found: C, 59.54; H, 7.72. The third component, R_f 0.38, mp 68–69 °C, was identified as **11** by comparison with an authentic sample.

Reduction of 16. A sample of **16** (30 mg, 0.1 mmol) was stirred with powdered zinc (1 g) in acetic acid (5 mL) at room temperature for 3.5 h. The zinc was filtered off and rinsed with ether (2 × 50 mL), and the combined ether layers were neutralized ($NaHCO_3$), dried ($MgSO_4$), and evaporated to give 22 mg (82% yield) of a yellow solid, mp 59–62 °C, identified as **11** by comparison of its IR, NMR, GC retention time, and mass spectrum with those of an authentic sample.

Registry No. **1**, 1129-21-1; **2**, 72526-01-3; **3**, 1947-24-6; **4**, 72526-02-4; **5**, 3383-21-9; **6**, 24289-60-9; **8a** (R = H), 67857-66-3; **8b**, 72526-03-5; **9a**, 67857-67-4; **9b**, 67857-69-6; **10**, 50521-99-8; **11**, 22961-94-0; **12a**, 72526-04-6; **12b**, 72526-05-7; **13a**, 72526-06-8; **13b**, 72526-07-9; **14a**, 72526-08-0; **14a'**, 61186-98-9; **16**, isomer 1, 72526-09-1; **16**, isomer 2, 72526-10-4; methanol, 67-56-1; $(PyCuOCH_3Cl)_2$, 15094-30-1.

Polyethers. 1. Preparation of ω,ω'-Bis(triphenylphosphine) Polyethers

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Although the title compounds seem to be important ligands in the formation of cyclic coordinated complexes with transition metals, relatively little attention has been given to the preparation of ω,ω'-bis(triphenylphosphine) polyethers from the corresponding dibromides.

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