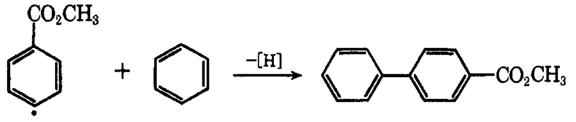
TABLE IV

ISOMER DISTRIBUTIONS FROM REACTION OF METHYL *p*-NITROBENZOATE WITH METHYL BENZOATE[a] AT 600°

Methyl biphenylcarboxylate isomer	1:5[b]	1:10
2	6	7
3	36	40
4	58	53
Dimethyl biphenyldicarboxylate isomer		
2,4′	9	12
3,4′	56	64
4,4′	35	24

[a] Conditions given in Table I. [b] Mole ratio methyl *p*-nitrobenzoate:methyl benzoate.

arylations. Isomer distributions of the methyl biphenylcarboxylates are difficult to interpret, as they may arise either from the reaction of a phenyl radical with methyl benzoate or from the interaction of a methyl benzoate radical ($CH_3O_2CPh\cdot$) with benzene. The high para percentage suggests the latter.



Differences in isomer distribution of arylation products, as well as differences in the nature of the products formed, provide a sharp contrast between free-radical attack on methyl benzoate in the gas phase *vs*. the liquid phase. Formation of phthalide from methyl benzoate by reaction with radicals in the gas phase represents a new type of intramolecular alkylation. This reaction is being studied further to extend its synthetic utility.

Registry No.—Methyl benzoate, 93-58-3; nitrobenzene, 98-95-3; methyl *p*-nitrobenzoate, 619-50-1.

Acknowledgment.—We acknowledge with thanks the assistance of D. K. Albert and S. Meyerson of the American Oil Company for gas chromatographic and mass spectrometric analyses.

A Novel Route to Bicyclo[2.2.2]octenetetracarboxylic Acid Dianhydrides

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Acetoxy-1,3-dienes, generated *in situ* from mesityl oxide, 2-cyclopentylidenecyclopentanone, 2-cyclohexenylcyclohexanone, and pulegone, undergo the Diels–Alder reaction with 2 equiv of maleic anhydride to yield bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride derivatives. Hydrolysis of dianhydrides **7** and **8** derived from 2-cyclopentylidenecyclopentanone and pulegone yields tetracarboxylic acids, whereas hydrolysis of dianhydrides **4** and **6** derived from mesityl oxide and 2-cyclohexenylcyclohexanone affords triacid lactone derivatives. Ozonolysis of tetramethyl ester **13** derived from **7** results in exclusive allylic oxidation yielding the unsaturated keto tetramethyl ester **15**, and lead tetraacetate oxidation of the corresponding tetraacid **12** occurs with participation of the carbon–carbon double bond affording a mixture of dilactones **16** and **17**.

Cyclic acetoxy 1,3-dienes, generated *in situ* from cyclic 1,2-, 1,3-, and 1,4-diketones, and from α,β-unsaturated ketones, react with maleic anhydride,[2] *p*-benzoquinone,[3] and dimethyl acetylenedicarboxylate[4] to yield oxygenated bicyclo[2.2.2]alkene derivatives. We have now extended this study to acyclic and exocyclic α,β-unsaturated ketones and find that reaction takes place with 2 equiv, rather than 1 of maleic anhydride to afford, instead of the expected acetoxy cyclohexenedicarboxylic anhydride,[5,6] bicyclo[2.2.2]oct-7-enetetracarboxylic acid dianhydride derivatives.

Heating mesityl oxide in isopropenyl acetate containing a catalytic amount of *p*-toluenesulfonic acid with 2.3 equiv of maleic anhydride affords 1,8-dimethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride (**4**). Dianhydride **4** was identified by spectral analysis and by comparison with an authentic sample of **4** prepared by the reaction of 4,6-dimethyl-2-pyrone with maleic anhydride.[7]

The bridgehead methyl group of adduct **4** exhibits a unique nmr resonance signal at δ 1.98 ppm which is at lower field than the vinyl methyl group which resonates at 1.78 ppm. Examination of molecular models indicates that the methyl group is in the deshielding cone of two rigidly held anhydride carbonyls. Hydrolysis of adduct **4** with sodium bicarbonate solution, followed by acidification with hydrochloric acid and esterification with diazomethane, gives trimethyl ester lactone **5**[8] in which the bridgehead methyl group is found at 1.0 ppm, a chemical shift which is normal for methyl attached to a saturated carbon atom. We attribute this change to the free rotation permitted for the carbonyl groups of the carbomethoxy groups and subsequent removal of the deshielding effect displayed by the dianhydride.

A plausible pathway for the formation of dianhydride **4** in the condensation of mesityl oxide with maleic anhydride is shown in Scheme I. 1,2 or 1,4 elimination of acetic acid from the initially formed monoadduct[9] would yield dienes **2** or **3**. Under the conditions of the reaction, dienes **2** and **3** might be inter-

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[1] David Ross Research Fellow, 1968–1969.

[2] C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

[3] J. Wolinsky and R. B. Login, *J. Org. Chem.*, **35**, 1987 (1970).

[4] J. Wolinsky and R. B. Login, *ibid.*, **35**, 3205 (1970).

[5] H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

[6] W. Flaig, *Justus Liebigs Ann. Chem.*, **568**, 1 (1950).

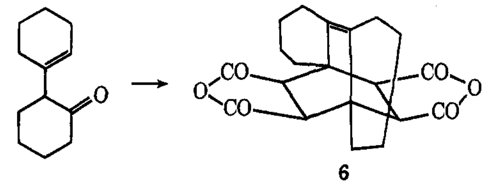
[7] O. Diels and K. Alder, *ibid.*, **490**, 259 (1931).

[8] Diels and Alder[7] reported the hydrolysis and esterification of **4** by this procedure and assigned the product, mp 155°, as a tetramethyl ester. The product we have isolated shows mp 153–154° and on the basis of its ir, nmr, and mass spectra is clearly trimethyl ester lactone **5**.

[9] P. Blanc, *Helv. Chim. Acta*, **44**, 1 (1961).

converted by a 1,5-hydrogen shift.[10] Diene **2** would be expected to react selectively[11] with maleic anhydride in the next Diels–Alder step to give adduct **4**.

2-Cyclohexenylcyclohexanone, 2-cyclopentylidenecyclopentanone, and pulegone also react with 2 equiv of maleic anhydride to form bicycloalkenedicarboxylic dianhydride derivatives **6**, **7**, and **8**, respectively.



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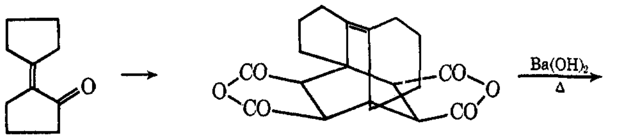

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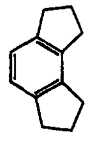

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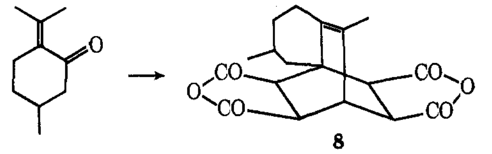
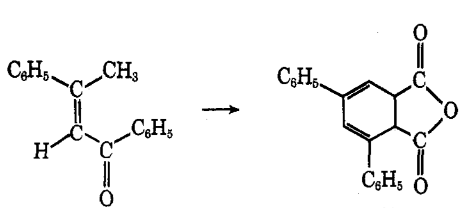


8

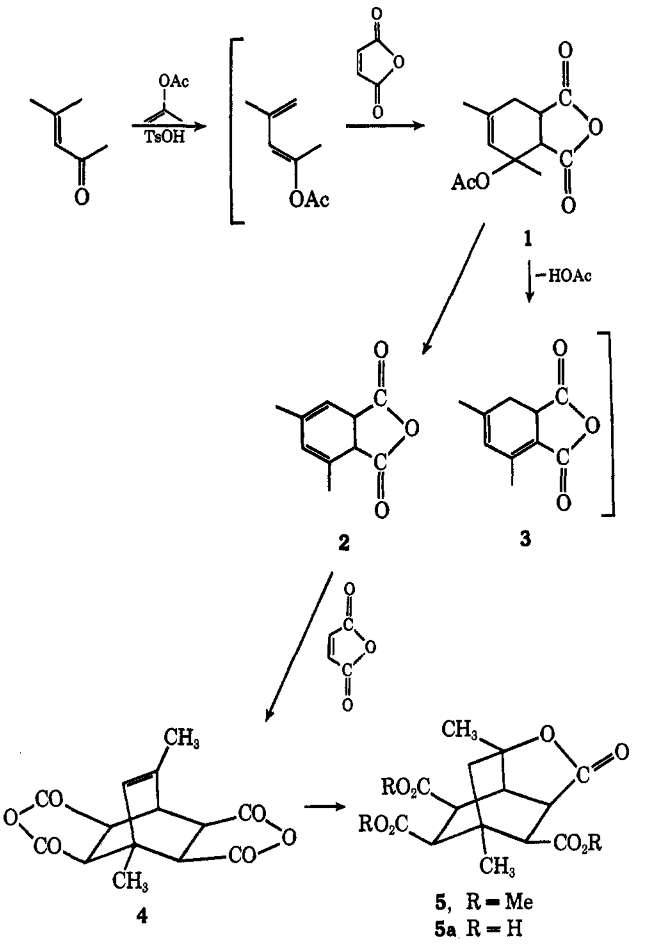
Adducts **6** and **7** display nmr singlets at 3.78 and 3.45 ppm, respectively, assigned to 4 HCCO protons; consequently, highly symmetrical structures are demanded for these adducts. This would not be the case if the adducts had been derived from a cyclohexadiene intermediate of structure related to diene **3**. Additional confirmation for the structure of adduct **7** was provided by its conversion on heating with barium hydroxide to hydrocarbon **9**. This latter transformation must involve a reverse Diels–Alder reaction followed by decarboxylation and aromatization.[12]

Dypnone (**10**) gave only a 1:1 adduct **11** with maleic anhydride. It is possible that the lower reactivity of **11** associated with the presence of two electron-withdrawing phenyl groups permits its isolation from the reaction mixture.

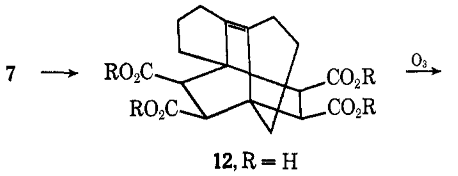


10 **11**

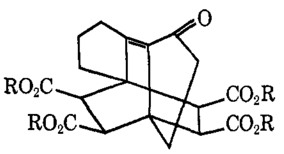
SCHEME I



We turn next to a description of some chemical transformations of adduct **7**. Hydrolysis of **7** with aqueous sodium bicarbonate, followed by acidification with hydrochloric acid, affords tetraacid **12** which, in turn, is converted into tetramethyl ester **13** by treatment with diazomethane. This behavior is similar to that observed with adduct **8**, but contrasts with the behavior of adducts **4** and **6** which are converted into trimethyl ester lactones **5** and **14** under similar conditions. Heating tetraacid **12** in acetic acid containing 5% sulfuric acid regenerated dianhydride **7**.



12, R = H
13, R = CH3



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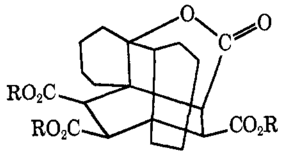

14

The carbon–carbon double bonds in all the dianhydrides are extremely hindered and do not decolorize bromine or reduce easily with hydrogen. Ozonolysis of **7** could not be performed because of its insolubility in common solvents; however, ozonolysis of tetramethyl ester **13** gave the conjugated keto tetramethyl ester **15**, providing dramatic illustration of the hindered nature of the double bond.

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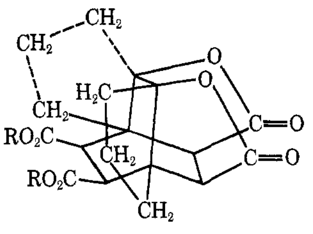
[10] J. Wolinsky, B. Chollar, and M. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).

[11] M. J. Goldstein, *ibid.*, **87**, 1925 (1965).

[12] See C. F. H. Allen and J. Van Allen, *J. Amer. Chem. Soc.*, **64**, 1260 (1942), for related transformations.

Oxidation of tetraacid **12** with lead tetraacetate[2] gave dilactones **16** and **17** which were isolated as their methyl esters following treatment with diazomethane. Participation of the double bond during lead tetraacetate oxidation[2] offers chemical evidence for the syn stereochemical assignment of the carboxyl groups relative to the carbon–carbon double bond.



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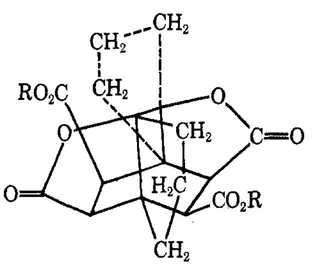
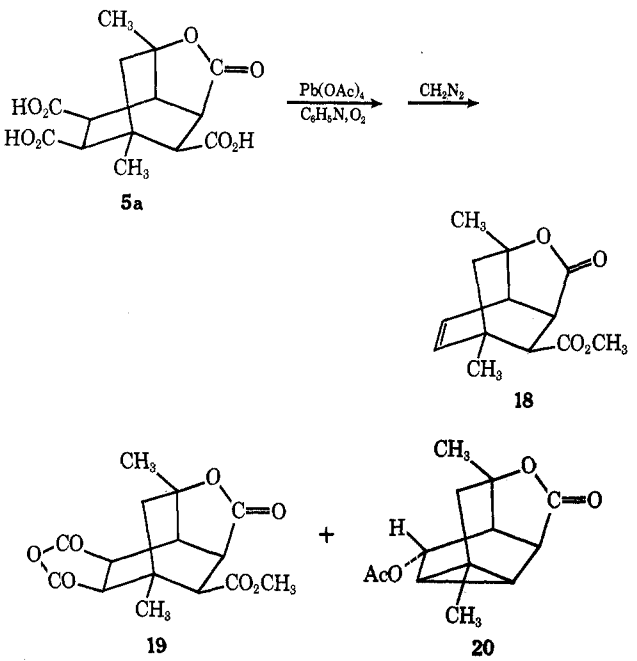
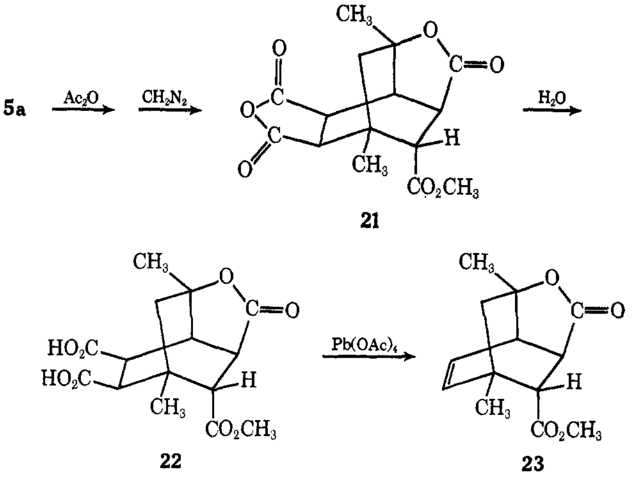


17

The action of lead tetraacetate on triacid lactone **5a** gave a complicated mixture which was separated into neutral and acidic fractions. The acid fraction was esterified with diazomethane and subjected to column chromatography. Unsaturated ester lactone **18** was isolated in pure form and identified on the basis of spectral considerations (see Experimental Section).



5a **18** **19** **20**



21 **22** **23**

Another amorphous fraction showed a molecular ion at m/e 308 and on the basis of its nmr and ir spectra was assigned structure **19**.

The neutral fraction contained at least three major components, only one of which was isolated in pure form and was assigned structure **20** on the basis of (1) elemental analysis and the appearance of a molecular ion at m/e 236; (2) an infrared spectrum which showed carbonyl absorption at 5.6 and 5.72 μ; and (3) a fit of the nmr spectrum with the proposed structure, including confirmation of the presence of an acetate group by the appearance of a signal at 2.08 ppm and the indication of two methyl groups by singlets at 1.06 and 1.41 ppm. The endo configuration of the acetate group was assigned on the basis of a singlet for the CHOAc proton at 5.04 ppm. Examination of molecular models indicates an approximate 90° dihedral angle between this proton and the adjacent bridgehead proton, requiring a very small spin–spin coupling constant, whereas appreciable spin coupling would have been anticipated if the acetate group were exo.

Heating triacid lactone **5a** with acetic anhydride, followed by esterification with diazomethane, gave the anhydride methyl ester **21**, whose nmr spectrum indicates that the carbomethoxy group is endo, epimerization apparently takes place during heating with acetic anhydride. Hydrolysis of anhydride **21** with water gave diacid methyl ester **22**, which was bisdecarboxylated in good yield to unsaturated ester lactone **23**. Treatment of unsaturated ester lactone **18** with sodium methoxide produced lactone **23**, establishing the configurational relationship between these two isomers.

From the array of products produced from triacid lactone **5a** and from the single product isolated from diacid methyl ester lactone **22** it is obvious that all three carboxyl groups are involved in the reaction of **5a** with lead tetraacetate. It seems reasonable to suggest that bisdecarboxylation of **5a** to acid **18a** is followed by a rapid reaction of lead tetraacetate to give acetate lactone **20**.[13]

Experimental Section[14]

1,8-Dimethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic Acid Dianhydride (4).—A stirred solution of 100 g of mesityl oxide and 230 g of maleic anhydride in 175 ml of isopropenyl acetate containing *ca.* 50 mg of *p*-toluenesulfonic acid was refluxed for 17 hr.[15] After cooling, part of the solvent was removed under diminished pressure, and cooling to −20° gave 144 g (52%) of crude adduct **4**, which was purified by recrystallization from acetonitrile: mp 270–272°; ir (KBr) 5.35 and 5.57 μ; nmr (C_6H_5CN) 1.78 (d, 3, J = 1 Hz, $CH_3C{=}C$), 1.98 (s, 3, CH_3C), 2.0–2.4 (broad m, impurity), 3.42 and 3.85 (distorted AB type quartet, 5), and 5.71 ppm ($HC{=}C$); mass spectrum (70 ev) m/e (rel intensity) 276 (28), 178 (73), 150 (56), 107 (23), 106 (59), 105 (32), 91 (100), 77 (25), 65 (25), 57 (23), 43 (28). No depression in melting point was observed when this sample was mixed with an authentic sample of dianhydride **4**, mp 272–274°.[7] The ir and nmr spectra were also identical with those of the authentic sample.

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[13] See N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, **85**, 3193 (1963), for a related transformation.

[14] All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrometer. Nmr spectra were measured with a Varian Associates A-60 spectrometer. The mass spectra were determined by the Purdue University Spectral Service Department employing a Hitachi RMU-6A mass spectrometer. Microanalyses were performed by Dr. C. S. Yeh and associates.

[15] *Caution:* Reactions run on this scale may require cooling if the reflux rate becomes too vigorous.

Trimethyl Ester Lactone 5.—A mixture of 2 g of dianhydride **4** and 20 ml of sodium bicarbonate solution was heated at reflux until the adduct dissolved (2–3 hr). The solution was cooled and concentrated hydrochloric acid was added resulting in the precipitation of 2.1 g of a white solid. The acid was dried *in vacuo*, dissolved in methanol, and treated with ethereal diazomethane. The solvents were evaporated to leave 2.3 g of crude ester lactone **5**. An analytical sample of **5** was prepared by recrystallization from ethanol: mp 153–154°; ir (Nujol) 5.65 and 5.75 μ; nmr ($CDCl_3$) 1.03 (s, 3, CCH_3), 1.68 (s, 3, CCH_3), 2.1 and 2.3 (m, 2), 3.06 (m, 5), 3.75 and 3.81 ppm (2s, 9, $-OCH_3$); mass spectrum (70 ev) *m/e* (rel intensity) 354 (3), 322 (13), 290 (6), 262 (5), 190 (8), 164 (14), 145 (30), 144 (100), 132 (13), 130 (10), 112 (77), 90 (33), and 58 (50).

Anal. Calcd for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.87; H, 6.42.

The same product (**5**) was obtained when adduct **4** was hydrolyzed by heating with water and the resulting acid esterified with diazomethane.

Dianhydride 6.—From 18.4 g of 2-cyclohexenylcyclohexanone[16] and 19.6 g of maleic anhydride in 60 ml of isopropenyl acetate there was obtained 10 g (26%) of crude adduct **6**. An analytical sample was obtained by recrystallization from acetonitrile: mp 308–310° (sealed tube); ir (Nujol) 5.4 and 5.6 μ; nmr (pyridine) 1.71 (m, 8), 2.16 (t, 4, $-CH_2C{=}C-$), 2.89 (t, 4), 3.78 ppm (s, 4, $CHC{=}O$); mass spectrum (70 ev) *m/e* (rel intensity) 356 (7), 328 (39), 300 (14), 230 (14), 229 (21), 186 (26), 185 (100), 158 (15), 143 (27), 129 (22), 128 (28), and 115 (22).

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.67; H, 5.75.

Hydrolysis of 1 g of adduct **6** with 10 ml of aqueous sodium bicarbonate solution, followed by acidification and esterification with diazomethane, gave 1.07 g (85%) of trimethyl ester lactone **14**. An analytical sample of **14** was obtained by recrystallization from benzene–hexane: mp 236–239°; ir ($CHCl_3$) 5.6–5.8 μ (broad); nmr ($CDCl_3$) 1.63 (m, 16), 2.5 (m, 2), 2.71 and 3.34 (AB q, 2, J = 13 Hz), 3.6 and 3.73 ppm (2s, 9, OCH_3).

Anal. Calcd for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96. Found: 63.43; H, 7.06.

Dianhydride 8.—From 100 g of pulegone and 150 g of maleic anhydride there was obtained 118 g (54%) of crude adduct **8**. A pure sample of **8** was obtained by recrystallization from acetonitrile: mp 327–328° (sealed tube); ir (Nujol) 5.4 and 5.6 μ; nmr [$(CD_3)_2SO$] 0.98 (d, 3, J = 6 Hz, $-CHCH_3$), 1.63 (s, 3, $C{=}CCH_3$), 2.32 (m, 4, $-CH_2-$), and 3.40 ppm (m, 5); mass spectrum (70 ev) *m/e* (rel intensity) 330 (43), 312 (4), 302 (15), 256 (8), 232 (13), 228 (15), 204 (69), 160 (31), 150 (100), 145 (20), 129 (13), 128 (13), 118 (20), 115 (13), 105 (13), and 91 (12).

Hydrolysis of dianhydride **8** with aqueous sodium bicarbonate, followed by acidification with hydrochloric acid and then esterification with diazomethane, afforded a tetramethyl ester which was recrystallized from benzene–hexane: mp 131–133°; ir (Nujol) 5.7 and 5.8 μ; nmr ($CDCl_3$) 0.88 (d, 3, CH_3), 1.0–1.8 (m, 5), 2.0 (s, 3, $C{=}CCH_3$), 2.4 (m, 2, $-CH_2C{=}C$), 2.89 and 2.99 (2s, 4, $-CHCO_2$), 3.22 (s, 1), and 3.56 (s, 12-OCH_3).

Anal. Calcd for $C_{22}H_{30}O_8$: C, 62.54; H, 7.16. Found: C, 62.40; H, 7.30.

Dianhydride 7.—From 10 g of 2-cyclopentylidenecyclopentanone[17] and 16.1 g of maleic anhydride there was obtained 13.5 g (62%) of dianhydride **7**. A pure sample of **7** was obtained by recrystallization from acetic anhydride: mp 317–318° (sealed tube); ir (Nujol) 5.4 and 5.6 μ; nmr [$(CD_3)_2SO$] 1.71 and 2.07 (m, 4, $C{=}CCH_2CH_2$), 2.58 (t, 4, $-CH_2-$), and 3.45 (s, 4, $-CHCO$) mass spectrum (70 eV) *m/e* (rel intensity) 328 (11), 298 (28), 270 (11), 229 (21), 202 (29), 201 (33), 158 (42), 157 (100), 129 (36), and 115 (24).

Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.91; H, 5.07.

Tetraacid 12.—A 2.0-g sample of dianhydride **7** was refluxed with 30 ml of aqueous sodium bicarbonate solution until solution occurred (2–3 hr). The solution was cooled and acidified with concentrated hydrochloric acid to give 1.8 g of tetraacid **12**, which was generally used without further purification.

A portion of tetraacid **12** was esterified with diazomethane to yield tetramethyl ester **13**. A pure sample of **13** was obtained by recrystallization from methanol: mp 223–224°; ir (Nujol) 5.72 μ; nmr ($CDCl_3$) 1.90 (broad s, 8, $-CH_2CH_2-$), 2.62 (broad s, 4, $-CH_2C{=}C$), 3.13 (s, 4, $-CHCO_2$), and 3.61 ppm (s, 12, $-OCH_3$).

Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C 63.00; H 6.92.

3,5-Diphenyl-1,2-dihydrophthalic Anhydride (11).—The reaction of 46.6 g of dypnone (**10**) and 50 g of maleic anhydride afforded an oil which was dissolved in a minimum amount of ethyl acetate, treated with Norit, filtered, and treated with hexane until some of the "tar" had precipitated. Upon cooling, 25 g (40%) of a yellow solid was isolated. Further recrystallization from ethyl acetate–hexane gave a pure sample of **11**: mp 158–159°; ir (Nujol) 5.42 and 5.62 μ; nmr ($CDCl_3$) 3.5 (m, 2) and 7.7 ppm (m, 12); mass spectrum (70 ev) *m/e* (rel intensity) 302 (4), 301 (18), 300 (78), 256 (61), 228 (70), 226 (41), 128 (100), and 44 (83).

Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.62; H, 4.76.

1,2,3,6,7,8-Hexahydro-*as*-indacene (9).—A mixture of 3 g of dianhydride **7** and 12 g of dry barium hydroxide[12] in a short path distilling apparatus was heated over a flame and after a few minutes 550 mg of material distilled (180–220°). This product was sublimed to give 520 mg (36%) of **9**: mp 38–38.5° (lit.[18] mp 40–42°); nmr ($CDCl_3$) 2.02 (m, 4), 2.75 (q, 8), and 7.0 ppm (s, 2).

Ozonolysis of Tetramethyl Ester 13.—A solution of 1.87 g of ester **13** in 30 ml of methylene chloride and 40 ml of acetic anhydride was ozonized at −78° for 30 min. The solution was added to 100 ml of water and 1 g of zinc dust and the mixture was stirred for 1 hr, filtered, and extracted with methylene chloride. The methylene chloride was washed with dilute sodium hydroxide solution, dried ($MgSO_4$), and evaporated to give 1.41 g (73%) of conjugated keto tetramethyl ester **15**. Recrystallization from acetone–hexane gave a pure sample of **15**: mp 201–202°; ir (Nujol) 5.71 and 6.01 μ; λ_{max}^{EtOH} 257 nm (ϵ 8000); nmr (pyridine) 1.82–3.5 (m's, 12), 3.50 and 3.51 ppm (2s, 12); mass spectrum (70 ev) *m/e* (rel intensity) 434 (21), 402 (6), 305 (8), 290 (13), 257 (19), 256 (11), 230 (24), 229 (36), 171 (26), 145 (13), 128 (9), 113 (100), and 59 (14).

Anal. Calcd for $C_{22}H_{26}O_9$: C, 60.82; H, 6.03. Found: C, 60.81; H, 5.99.

Lead Tetraacetate and Tetraacid 12.—Oxygen was bubbled for 15 min through a solution of 7.46 g of tetraacid **12** in 75 ml of pyridine and then 50 g of lead tetraacetate was added at one time. The mixture was heated to 60°, turned light orange and after several minutes boiled violently, turning dark brown. Stirring was continued for 1 hr, at which time the mixture was cooled, poured into dilute nitric acid, and extracted with ether. The ether extracts were washed with brine solution, dried ($MgSO_4$) and evaporated, leaving an oil which was triturated with ether to give 1.2 g of solid. This solid was treated with ethereal diazomethane to give dimethyl ester dilactone **16**, which was recrystallized from chloroform–hexane: mp 233–235°; ir 5.6 and 5.75 μ; nmr ($CDCl_3$) 2.0 (m, 12), 2.81 and 3.29 (AB q, 4, J = 9 Hz, CHCO), 3.75 ppm (s, 6, $-OCH_3$); mass spectrum (70 ev) *m/e* (rel intensity) 390 (42), 358 (47), 314 (61), 260 (36), 216 (49), 215 (80), 157 (100), 155 (57), 131 (37), 129 (40), 115 (36), 113 (34), 91 (33), 59 (42), and 55 (39).

Anal. Calcd for $C_{20}H_{22}O_8$: C, 61.54; H, 5.68. Found: C, 61.65; H, 5.54.

Evaporation of the ether solution obtained by trituration of the crude reaction product left 2.3 g of oil. A 1.0-g portion of this material was treated with ethereal diazomethane and the resulting oil was chromatographed on silica gel. Elution with hexane–ethyl acetate gave several fractions, the second of which solidified when triturated with ether to give 400 mg of solid dilactone **17**, which was recrystallized from chloroform–hexane: mp 201–202°; ir (Nujol) 5.6 and 5.8 μ; nmr ($CDCl_3$) 2.0 (m, 12), 2.84 (broad s, 3, $-CHCO$), 3.03 (s, 1, $-CHCO$), 3.65 and 3.71 ppm (2s, 6, $-OCH_3$); mass spectrum (70 ev) *m/e* (rel intensity) 390 (9), 359 (28), 358 (100), 314 (9), 286 (7), 258 (9), 215 (10), 210 (14), 157 (20), 131 (10), 129 (13), 115 (12), 91 (12), 59 (16) and 55 (14).

Anal. Calcd for $C_{20}H_{22}O_8$: C, 61.54; H, 5.68. Found: C, 61.24, H, 5.75.

Lead Tetraacetate and Trimethyl Ester Lactone 5a.—Oxygen was bubbled through a stirred solution of 5.0 g of trimethyl

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[17] R. Meyer, *ibid.*, **89**, 1443 (1956).

[18] H. Rapoport and G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 1171 (1960).

ester lactone **5a** in pyridine and then 16 g of lead tetraacetate was added at once. The mixture was heated to 65° and, after a 2–3-min induction period, carbon dioxide evolution began and became quite vigorous. After carbon dioxide evolution ceased (3 min), stirring was continued for 5 min, and the mixture was cooled and then poured into dilute nitric acid. The resulting mixture was extracted with ether. The ether extracts were washed with brine solution, concentrated to 100 ml, and then extracted with saturated sodium bicarbonate solution. The neutral ether solution was washed with brine solution and dried ($MgSO_4$), and the ether was evaporated to leave 620 mg of oil. Thick layer chromatography on silica gel employing hexane–ether–ethyl acetate (10:1:3) gave 400 mg of oil as the fastest moving component. The oil was rechromatographed on silica gel using hexane–ethyl acetate (1:1) to develop the plate and afforded 310 mg in the fastest moving fraction. Recrystallization from benzene–hexane gave 240 mg of acetate lactone **20**: mp 95.5–97.5°; ir ($CHCl_3$) 5.6 and 5.72 μ; nmr ($CDCl_3$) 1.06 and 1.41 (2s, 6, $-CH_3$), 1.63 (m, 2), 1.92 (s, 2, $-CH_2$), 2.08 (s, 3, $-OCOCH_3$), 2.62 (d, 1, J = 6 Hz C_4 H), 3.03 and 3.12 (d of d, 1 J = 6 and 4 Hz, C_5 H), and 5.04 ppm (s, 1, C_3 H); mass spectrum (70 ev) m/e (rel intensity) 236 (6), 194 (3), 176 (3), 150 (4), 133 (7), 132 (8), 106 (9), 91 (7), 87 (10), 85 (66), 83 (100), 43 (15).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.29; H, 6.86.

The sodium bicarbonate solution obtained above was neutralized with hydrochloric acid and extracted with ether. The ether extracts were washed with brine solution, dried ($MgSO_4$), and evaporated to afford an oil which was esterified with diazomethane to yield 0.92 g of a viscous oil. A 278-mg sample of this oil was subjected to thick layer chromatography using silica gel and 1:1 hexane–ethyl acetate as a developer. The fastest moving component, 35 mg, proved to be unsaturated ester lactone **18** and was purified by recrystallization from benzene–hexane: mp 72–73°; ir ($CHCl_3$) 5.6 and 5.75 μ; nmr ($CDCl_3$) 1.0 and 1.23 (d of d, 1, J = 2 and 15 Hz, C_7 H), 1.20 and 1.38 (2s, 6, CH_3), 2.23 and 2.42 (d of d, 1, J = 1.5 and 10 Hz, C_5 H), 2.68 (d, 1, J = 15 Hz, C_7 H), 2.65 (broad s, 1, C_6 H), 3.18 (m, 1 C_4 H) 3.71 (s, 3, $-OCH_3$), and 6.20 ppm (m, 2, CH=CH); mass spectrum m/e (rel intensity) 236 (71), 208 (95), 205 (15), 176 (20), 161 (31), 151 (84), 149 (77), 148 (20), 133 (20), 119 (16), 107 (96), 106 (41), 105 (52), 92 (30), 91 (100), 79 (19), 77 (21), 65 (18), 59 (26), and 43 (82).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: 66.30; H, 6.83.

The next fastest moving component isolated from tlc, 117 mg, proved to be a mixture and could not be separated by additional thin layer chromatography. The mixture showed four $-OCH_3$ singlets at 3.70, 3.73, 3.78, and 3.80 ppm and a molecular ion in its mass spectrum at m/e 294 (20) and important ions at m/e 266 (20), 175 (28), 165 (21), 133 (38), 106 (23), 105 (32), 91 (28), 85 (65), 83 (100). This mixture was not characterized further.

The slowest moving component, 70 mg, proved to be **19** as indicated by ir bands at 5.62 and 5.75 μ and a molecular ion at m/e 308.

Lead Tetraacetate and Diacid Lactone 22.—Diacid lactone **22** was obtained by heating 4.5 g of triacid lactone **5a** with 40 ml of acetic anhydride for 1–2 hr. The excess anhydride was removed under diminished pressure and the resulting solid, mp 280–285°, was treated with excess diazomethane in ether. Evaporation of the ether gave 4.2 g of an oil which was heated with 30 ml of water until solution occurred (2 hr). The ether was evaporated under diminished pressure to leave 4 g of **22** as a viscous oil, which was used directly in the next step.

The crude **22** was dissolved in pyridine and oxygen was bubbled through the solution for 15 min. Lead tetraacetate (12 g) was added at once and the mixture was immediately placed in an oil bath maintained at 70°. After 2–3 min carbon dioxide evolution began. When bubbling ceased the mixture was cooled and worked up in the usual fashion to give 1.03 g of neutral oil. Column chromatography of 0.8 g of this oil on silica gel and elution with hexane–ethyl acetate gave 70 mg of unidentified oil and 600 mg of unsaturated ester lactone **23**. The analytical sample was secured by recrystallization from pentane: mp 53–55°; ir ($CHCl_3$) 5.62 and 5.75 μ; nmr ($CDCl_3$) 1.23 and 1.80 (AB q, 2, J = 14 Hz, C_7 H), 1.34 (s, 6, $-CH_3$), 2.6 (d, 1, J = 1.5 Hz, $-CHCO_2$), 2.77 and 2.86 (d of d, 1, J = 9 and 1.5 Hz, C_5 H), 3.18 (q, 1, J = 4 Hz, C_4 H), 3.68 (s, 3, $-OCH_3$), and 6.18 (d, 2, CH=CH).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: 66.23; H, 6.82.

The acid fraction isolated in the work-up of the above reaction gave 1.1 g of oil. Chromatography of 800 mg of this material on silica gel and elution with hexane–ethyl acetate gave 150 mg of anhydride **21**, while later fractions (0.6 g) when heated with acetic anhydride gave an additional 350 mg of anhydride **21**: mp 179–180.5°; ir ($CHCl_3$) 5.39, 5.6, and 5.79 μ; nmr ($CDCl_3$) 1.38 and 1.44 (2s, 6, $-CH_3$), 1.73 (s, 1, C_7 H), 1.83 (d, 1, J = 2 Hz, C_7 H), 2.66 (s, 1, C_6 H), 2.99 (broad, s, 2), 3.00 and 3.19 (m, 1), 3.77 ppm (s, 3, $-OCH_3$); mass spectrum (70 eV) m/e (rel intensity) 308 (20), 290 (7), 277 (7), 264 (17), 236 (6), 205 (7), 192 (13), 177 (12), 165 (100), 151 (20), 133 (49), 121 (16), 119 (15), 107 (15), 91 (27), and 43 (36).

Anal. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 58.61; H, 5.18.

Epimerization of Unsaturated Ester Lactone 18.—A solution of 60 mg of **18** in methanol containing *ca.* 40 mg of sodium methoxide was kept at ambient temperature for 12 hr. Water and hydrochloric acid were added and the mixture was extracted with ether. Work-up of the ether solution gave an oil which was recrystallized from pentane to give a solid, mp 47–50°, whose spectral properties were identical with those of unsaturated ester lactone **23**.

Registry No.—**4**, 32251-35-7; **5**, 32251-36-8; **6**, 32251-37-9; **7**, 32304-26-0; **8**, 32251-38-0; **9**, 1076-17-1; **11**, 25278-11-9; **13**, 32251-41-5; **14**, 32251-42-6; **15**, 32251-43-7; **16**, 32237-59-5; **17**, 32237-60-8; **18**, 32304-27-1; **20**, 32251-44-8; **21**, 32251-45-9; **23**, 32251-46-0; tetramethyl ester, mp 131–132°, 32251-47-1.