lization from methanol afforded the pure diester **1b** as colorless prisms: mp 86–87°; ir (CCl_4), 1740 (ester C=O) and 1660 cm^{-1} (weak, C=C); uv maxima, 266 mμ (ε 274), 270 (shoulder, 223), and 274.5 (200); nmr (CCl_4), δ 6.7–7.2 (3 H multiplet, aryl CH), 5.1–5.9 (2 H multiplet, vinyl CH), 4.0–4.3 (1 H multiplet, benzylic CH), 3.79 (1 H singlet, benzylic CH), 3.63 (3 H singlet, OCH_3), 3.53 (3 H singlet, OCH_3), 2.28 (3 H singlet, aryl CH_3), and 1.6–2.9 (4 H multiplet, aliphatic CH); mass spectrum, molecular ion peak at *m/e* 300, abundant fragment peaks at *m/e* 181, 180, 166, and 165.

Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.86; H, 6.81.

A solution of 172 mg (0.51 mmol) of the diester **1b** and the sodium methoxide from 75 mg (3.3 mg-atom) of sodium in 3.0 ml of methanol-d_1 was refluxed for 3 days and poured into a mixture of deuterium oxide and acetic acid-d_1. The resulting mixture was concentrated under reduced pressure and an ether solution of the residue was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated to leave 159 mg (93%) of the crude partially deuterated diester **1b**, mp 76–82°. Recrystallization from methanol afforded 94 mg of the ester **1b**, mp 84–85°, which contained 16% d_0 species and 84% d_1 species. The nmr spectrum of this material corresponded to the spectrum previously described except that the singlet at δ 3.79 (benzylic CH) was markedly reduced in intensity.

A mixture of 1.064 g (3.08 mmol) of the etherate of the diacid **1a** and 632 mg of a 30% palladium-on-carbon catalyst was heated to 235° under a slow stream of nitrogen for 2.25 hr. The resulting mixture was extracted with boiling chloroform and the chloroform extract was filtered and concentrated. Recrystallization of the residual white solid from ethanol separated 243 mg (50.5%) of 1-methylfluorene (**18**) as white prisms, mp 83–84.5°; after sublimation at 80° (3 mm), the material melted at 85–87° (lit. mp 85°,[18a] 86°[18b]).[19] This material was identified with a subsequently described sample by a mixture melting point determination and by comparison of infrared and mass spectra.

To obtain an authentic sample of the fluorene **18**, a 300-mg (1.76 mmol) sample of the ketone **19**[20] was reduced with 1.5 ml of hydrazine hydrate and 0.60 g (11 mmol) of KOH in 20 ml of diethylene glycol for 3 hr at 175° and 0.5 hr at 250°. The crude neutral product (180 mg), isolated in the usual way, was recrystallized from ethanol to separate 120 mg of the fluorene **18**, mp 83.6–85.6°. After sublimation at 70° (0.2 mm), the product melted at 85–86°.

Preparation of the Anhydride 17.—The ether solvate of the diacid **1a** (1.448 g or 4.19 mmol) was distilled twice in a short-path still (0.2 mm and 180–190° bath) to yield 1.010 g (84%) of the anhydride **17** as a colorless liquid. The anhydride **17** crystallized on standing as white prisms: mp 99.6–101.6°; ir (CCl_4), 1790 and 1855 cm^{-1} (anhydride C=O in a five-membered ring); uv maxima (CH_3CN), 265 mμ (ε 307), 270 (shoulder, 246), and 274 (238); nmr ($CDCl_3$), δ 6.9–7.3 (3 H multiplet, aryl CH), 5.8–6.0 (2 H multiplet, vinyl CH), 4.29 (1 H singlet, benzylic CH), 3.84–4.1 (1 H multiplet, benzylic CH), 2.52 (3 H singlet, aryl CH_3), and 2.2–2.9 (4 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.70; H, 5.59.

A solution of 254 mg (1.0 mmol) of the anhydride **17** in 10 ml of methanol was refluxed for 3 hr and then concentrated under reduced pressure. The residual monomethyl ester(s) was esterified with excess ethereal diazomethane. The crude neutral product was recrystallized from methanol to separate 130 mg (43%) of the diester **1b**, mp 85–88°, identified with the previously described sample by a mixture melting point and comparison of infrared spectra. An additional 50 mg (17%) of the diester **1b**, mp 85–87°, was recovered from the mother liquor.

Registry No.—**1a**, 15448-20-1; ether solvate of **1a**, 15448-21-2; **1b**, 15448-22-3; **1b**, *C-9-d_1*, 15544-45-3; **3**, 15448-23-4; **10**, 15448-24-5; **15**, 15448-25-6; **16a**, 15448-29-0; **16**, 15448-26-7.

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[18] (a) L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, **68**, 751 (1946); (b) W. C. Lothrup and P. A. Goodwin, *ibid.*, **65**, 363 (1943).

[19] The other possible product would have been 4-methylfluorene (**21**) which is reported to melt at 71.5–72.5° [M. Orchin and E. O. Woolfolk, *ibid.*, **67**, 122 (1945); and 70.4–71.2° [L. J. E. Hofer and W. C. Peebles, *Anal. Chem.*, **23**, 690 (1951)].

[20] H. O. House, R. G. Carlson, H. Müller, A. W. Noltes, and C. D. Slater, *J. Amer. Chem. Soc.*, **84**, 2614 (1962).

Perhydroindan Derivatives. X. The Diels–Alder Reaction with 6-Methoxyindene Derivatives[1a]

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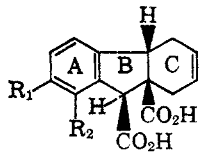
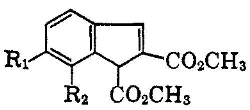
Both of the double-bond isomers of 1,2-dicarbomethoxy-6-methoxyindene (**4** and **17**) and 1,2-dicarbomethoxyindene (**19** and **20**) have been synthesized. In each case the less highly substituted double isomer **4** or **20** is the more stable. However, derivatives of each of these indenes react with 1,3-butadiene to give the Diels–Alder adduct derived from the more highly substituted double-bond isomer.

As noted in the accompanying paper,[2] we wished to synthesize the tetrahydrofluorene diacids **1** and **2** as



1, $R_1 = H$; $R_2 = CH_3$
2, $R_1 = OCH_3$; $R_2 = H$



3, $R_1 = H$; $R_2 = CH_3$
4, $R_1 = OCH_3$; $R_2 = H$

potential precursors for epiallogibberic acid and gibberellin derivatives in which the A ring is nonaromatic. It was our intention to use the indenes **3** and **4** as reactants with 1,3-butadiene to produce these acids **1** and **2**. The accompanying paper[2] describes the successful conversion of the indene **3** into the diacid **1**. In this manuscript, we describe the synthesis of the indene **4**. However, the reaction of this indene **4** with 1,3-butadiene did not yield the desired diacid **2**, but rather a structurally isomeric product.

The synthetic route (Scheme I) used for the indene derivative **4** followed the general pattern described[2] for the indene **3**. Differences were observed in the Friedel–Crafts cyclization of the anhydride **9** where the major product **11** was accompanied by lesser amounts (10–20%) of the alternative cyclization product **10**. The structure of the major product **11** was confirmed by oxidation to form the known phthalic acid derivative **12**. Unlike the result obtained in the previous study[2] with the 7-methylindanone derivative, the keto diester

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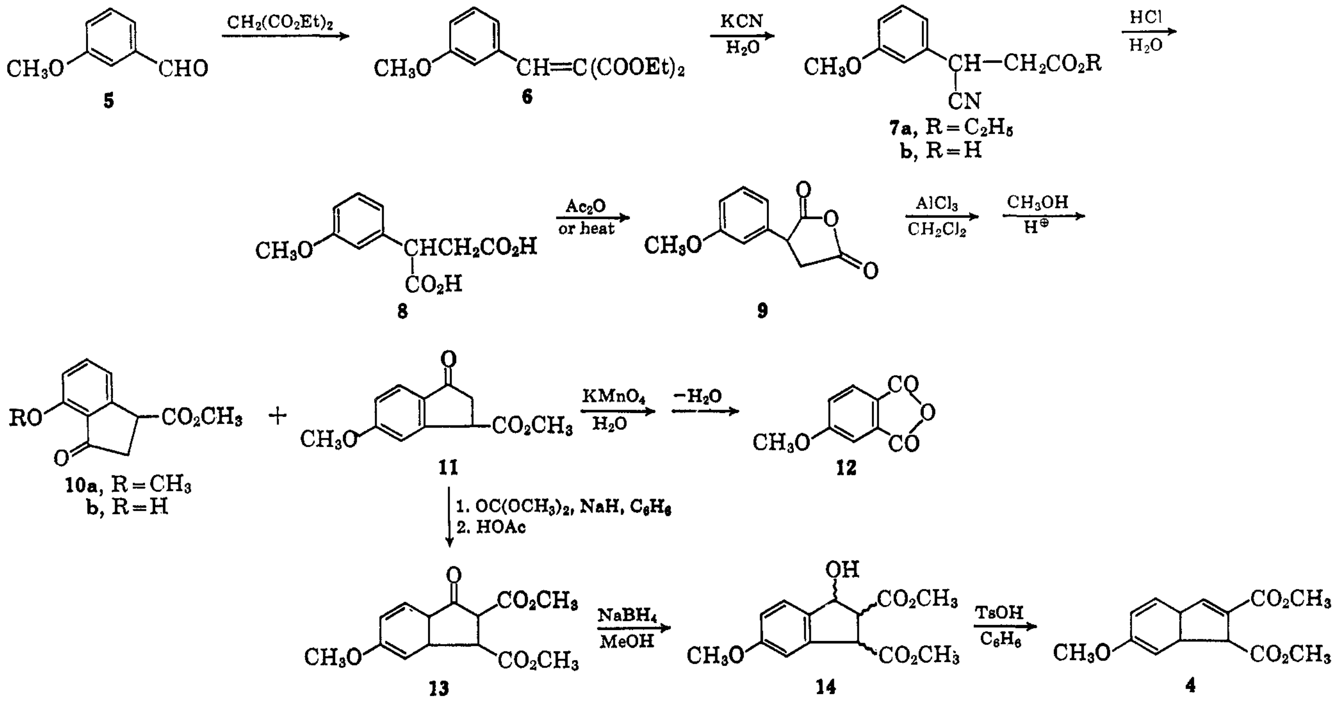
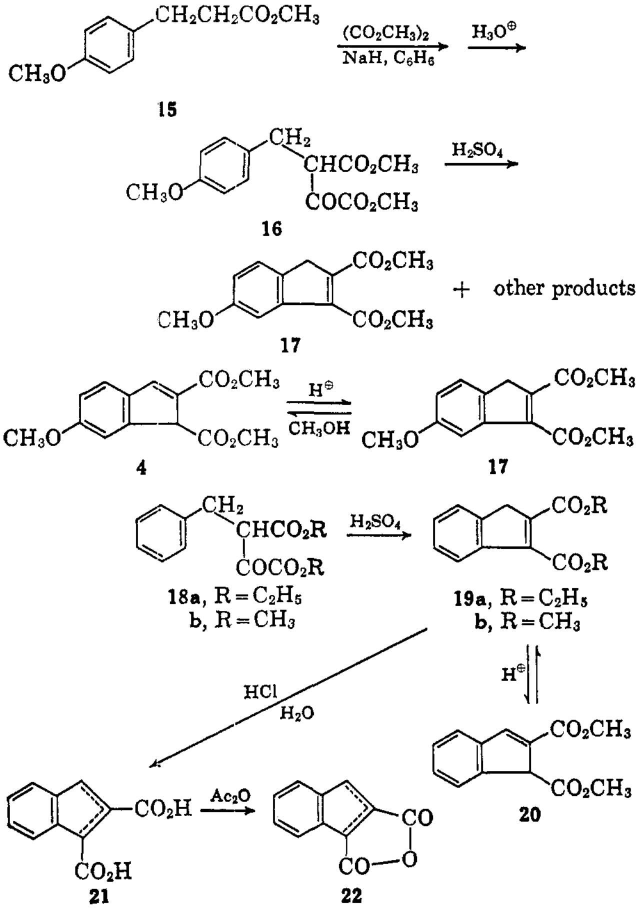
[1] (a) This research has been supported by grants from the National Science Foundation (Grant No. GP-5685) and the National Institutes of Health (Grant No. GM-08761); (b) National Institutes of Health Predoctoral Fellow, 1964–1967.

[2] H. O. House, F. J. Sauter, W. G. Kenyon, and J. J. Riehl, *J. Org. Chem.*, **33**, 957 (1968).

Scheme I



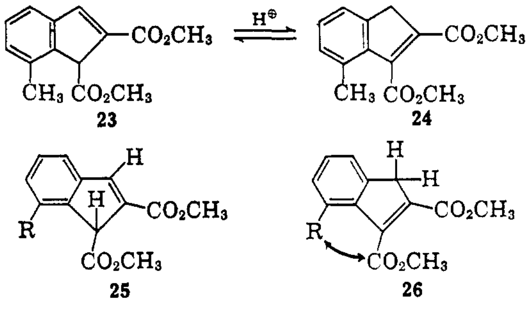
Scheme II



13 could be successfully reduced to the alcohol **14** with sodium borohydride at low temperatures (−35°). Acid-catalyzed dehydration yielded the desired indene **4**.

Although nmr data established that the product from this reaction sequence (Scheme I) had the structure **4** rather than **17**, it was also pertinent to learn which isomer, **4** or **17**, was more stable. An authentic sample of the second double-bond isomer **17** was obtained in poor yield by the sulfuric acid catalyzed cyclization of the crude keto diester **16** (Scheme II). This synthesis was patterned after the cyclization[3] of the keto diester **18a** to form the unsaturated diester **19a**, a report which we confirmed by converting both keto diesters **18** into the unsaturated esters **19**. The acid-catalyzed equilibration of each of the pairs of dimethyl esters **4** and **17** and **19b** and **20** established that in both cases the less highly substituted isomers **4** and **20** were the more stable and constituted 85–95% of the equilibrated mixtures. This result corresponds to the previously reported finding[2] that the mixture obtained from treatment of the unsaturated diester **23** with acid contains at least 95% of the less highly substituted olefin **23** (Scheme III). The positions of these equilibria are understandable if one considers structures **25** and **26** for the two types of olefins. Only in the more highly substituted olefins **26** must one of the carbomethoxy groups be eclipsed (heavy arrow in **26**) with the *ortho* substituent R. This steric destabilization should be more important in the diester **24** where R = CH_3 (structure **26**) than in the cases **17** and **19b** where R = H

Scheme III



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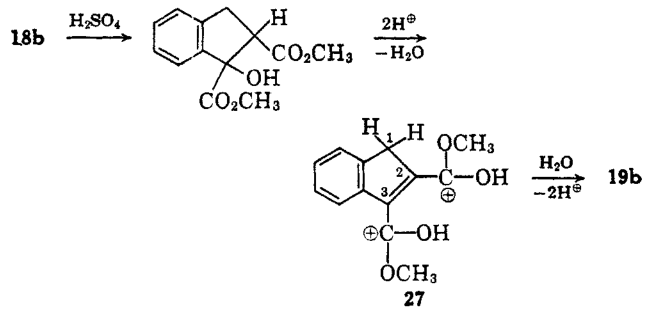
[3] (a) V. R. Skvarchenko, L. A. Chervoneva, and R. Ya. Levina, *J. Gen. Chem. USSR*, **30**, 52 (1960); (b) J. Bougault, *Compt. Rend.*, **159**, 745 (1914).

(structure 26), an expectation which is in agreement with the positions of the three equilibria. Contrary to earlier reports,[3] we found that hydrolysis of diester **19a** yielded a mixture of diacids **21** in which the less highly substituted isomer predominated. Also, the anhydride **22** produced from this diacid **21** was a mixture of isomers which gave a mixture of 66% **20** and 34% **19b** when treated successively with methanol and with diazomethane.

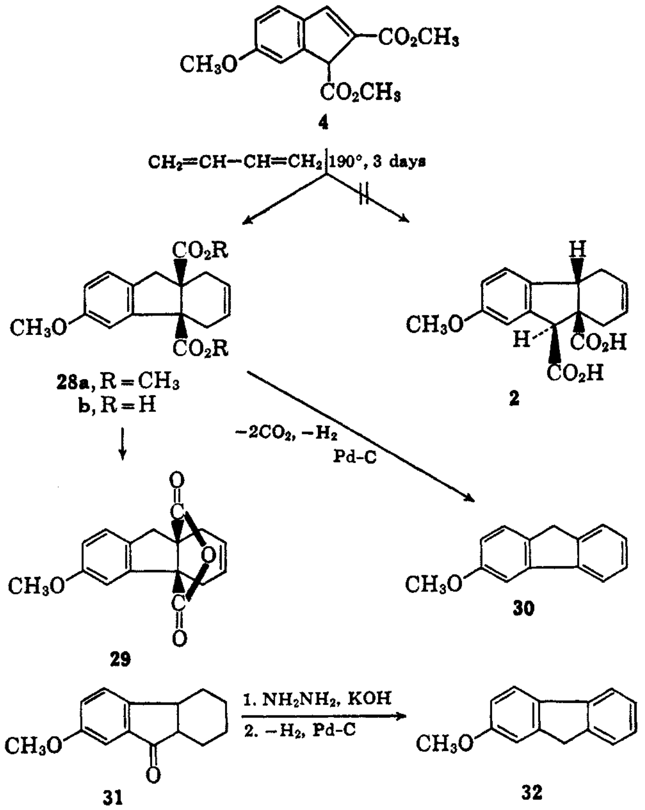
Since each of these pairs of unsaturated esters is readily equilibrated by a methanolic solution of *p*-toluenesulfonic acid, it is of interest that only the *less stable* isomers **17** and **19** were isolated from reaction of the keto esters **16** and **18** with concentrated sulfuric acid. To demonstrate that this result should not be attributed simply to a different equilibrium position for the protonated derivatives of these diesters, a mixture of *ca.* 95% of **20** and *ca.* 5% **19b** was dissolved in concentrated sulfuric acid and then quenched in an ice–water mixture. The composition of the recovered mixture of esters **19b** and **20** was not altered significantly. Instead, we believe these cyclization results are better explained by assuming that the protonated olefinic diester (*e.g.*, **27**, Scheme IV) initially formed in the reaction mixture is not isomerized because there is no good base (*e.g.*, water, unprotonated ketone) present in the concentrated sulfuric acid to remove a proton from C-1,[4] a required step in the isomerization process. Presumably, the subsequent process of quenching the reaction mixture in an ice–water mixture does not provide time for the relatively slow abstraction of a proton from carbon[5] to compete with the rapid transfer of protons bound to oxygen.

SCHEME IV



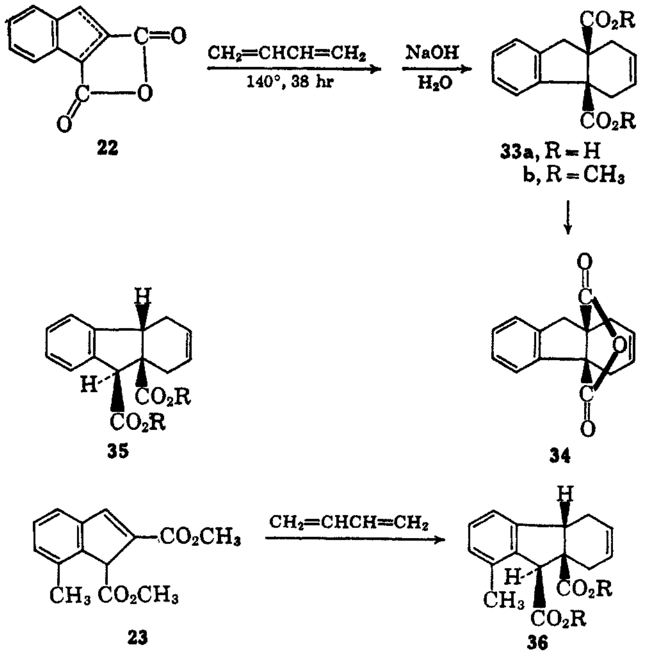
Reaction of the more stable unsaturated ester **4** with 1,3-butadiene (Scheme V) required relatively vigorous conditions which lead to a substantial amount of diene polymerization accompanying the desired Diels–Alder reaction. From this reaction, we were successful in isolating only a single adduct **28** in yields of 40% or less. Both the nmr spectrum of the anhydride **29** derived from this adduct **28b** and decarboxylation and dehydrogenation of **28b** to 3-methoxyfluorene (**30**) rather than the isomer **32** established the structure of this adduct as **28** rather than the desired structure **2**. We must therefore conclude that under all of the various conditions where we studied this Diels–Alder reaction the isomerization **4** ⇌ **17** was more rapid than subsequent Diels–Alder reaction and the less stable olefin **17** was evidently the more reactive dieneophile.

SCHEME V



Earlier workers[3a] had reported that the product derived from treating the anhydride **22** with ethanol[6] underwent a Diels–Alder reaction with 2,3-dimethyl-1,3-butadiene to form an adduct **33** analogous to structure **28** (Scheme VI). However, they offered no evidence which would have distinguished between structures of the types **33** and **35** for their adduct. We there-

SCHEME VI



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(4) For related examples, see (a) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, **82**, 1457 (1960); (b) C. G. Swain, and A. S. Rosenberg, *ibid.*, **83**, 2154 (1961).

(5) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(6) Although the authors (ref 3a) described this material as an ethanol solvate of the anhydride **22**, we think it probable that they were working with one or more isomeric monoethyl esters.

fore examined this Diels–Alder reaction of 1,3-butadiene with the mixture of anhydrides **22** (mainly the less highly substituted olefin) and were able to isolate, after hydrolysis, only a single adduct **33a**. Examination of the nmr spectra of this adduct **33** and the related anhydride **34** verified the structure of the adduct as **33** and not **35**. Therefore, this reaction also appears to involve prior isomerization of the dienophile and preferential reaction of the less stable isomer with the diene to form the predominant, if not exclusive, adduct.

It is therefore apparent that the successful conversion of the 7-methylindene derivative **23** to the "expected" Diels–Alder adduct **36** is exceptional. Apparently in this case the *o*-methyl substituent in the dienophile **23** provides sufficient destabilization of the isomeric diester **24** (see structure **26** where R = CH_3), that reaction of the diene occurs primarily, if not exclusively, with the isomer **23**.

Experimental Section[7]

Ethyl β-(*m*-Methoxyphenyl)-β-cyanopropionate (7a).—*m*-Hydroxybenzaldehyde was methylated by the general procedure previously described[8] to form the methoxy aldehyde **5**, in 94.5% yield: bp 68–72° (0.6 mm); n^{25}D 1.5527 [lit.[8] bp 88–90° (3 mm)]; uv maxima, 218 mμ (ϵ 21,500), 252 (9470), and 313 (2770). Following the general procedure described elsewhere,[9] this aldehyde **5** was converted into the arylidene malonate **6** in 95% yield as a pale yellow oil, bp 167–170° (0.6 mm) [lit.[13] bp 160° (0.003 mm)], which solidified on standing, mp 40–44°. Recrystallization from cyclohexane afforded the pure diester **6** as white prisms: mp 44–44.5°; ir (CCl_4), 1730 (ester C=O) and 1635 cm^{-1} (conjugated C=C); uv maxima, 213 mμ (ϵ 12,000), 234 (9120), and 280 (13,400); nmr (CCl_4), δ 7.48 (1 H singlet, vinyl CH), 6.6-7.3 (4 H multiplet, aryl CH), 4.18 (4 H quadruplet, J = 7 cps, $-CH_2O$), 3.68 (3 H singlet, CH_3O), 1.20 and 1.26 (6 H overlapping triplets, J = 7 cps for each, CH_3C).

Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.65; H, 6.59.

Reaction of 362 g (1.3 mol) of the arylidene malonate **6** with potassium cyanide, following a previously described procedure[11] except that the reaction mixture was not acidified, yielded 228 g (75.2%) of the cyano ester **7a** as a pale yellow oil: bp 164–166° (0.6 mm), $n^{21.5}$D 1.5100; ir (CCl_4), 2240 (C≡N) and 1740 cm^{-1} (ester C=O); uv maxima, 222 mμ (ϵ 7230), 274 (2370), and 281 (2190); nmr (CCl_4), δ 6.4–7.4 (4 H multiplet, aryl CH), 3.9–4.4 (3 H multiplet, $-CH_2O$ and benzylic CH), 3.74 (3 H singlet, OCH_3), 2.78 (2 H, center of multiplet, $-CH_2CO_2R$), and 1.22 (3 H triplet, J = 7 cps, CH_3C).

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 67.26; H, 6.49; N, 5.87.

The aqueous washings from this procedure[11] were found to contain the salt of a partially hydrolyzed product. Accordingly, the crude acidic product (**7b**, 58.5 g) recovered from the aqueous phase was hydrolyzed with aqueous HCl as subsequently described to yield 34.2 g (11.8%) of the succinic acid **8**, mp 175–179° dec.

α-(*m*-Methoxyphenyl)succinic Anhydride (9).—A mixture of 354 g (1.52 mol) of the cyano ester **7a**, 600 ml of concentrated aqueous HCl, and 3100 ml of water[12] was refluxed for 18 hr, cooled to 85°, treated with 500 ml of toluene, and then cooled to 5° with stirring.[13] The diacid **8**, collected on a filter and washed successively with cold water and with toluene, amounted to 280.5 g (82.5%) of white prisms: mp 177–178° dec; ir (KBr pellet), 1710 cm^{-1} (carboxyl C=O).

The combined toluene extracts from the hydrolysis of 3020 g (12.9 mol) of cyano ester **7a** were concentrated and a benzene solution of the residue (363 g of brown oil) was extracted with aqueous $NaHCO_3$ to separate, after appropriate manipulations, 269 g of crude acidic product as a pale yellow oil. A 255-g portion of this crude product was saponified with refluxing aqueous 10% NaOH to yield, after acidification and extraction of colored materials with benzene, an additional 204 g (7.1%) of the crude acid **8**, mp 170–175° dec.

A mixture of 203 g (0.90 mol) of the diacid **8** and 250 ml of acetic anhydride was heated to 90° with stirring until a solution was obtained. The resulting solution was concentrated under reduced pressure and the residual oil was crystallized from a benzene–cyclohexane mixture to separate 116 g of the anhydride **9** as white prisms, mp 65–67°. The material from the mother liquors was distilled [bp 185–195° (1 mm)] and then recrystallized to separate an additional 24 g (total yield 140 g or 75%) of the anhydride **9**: mp 65–67°; ir (CCl_4), 1870 and 1790 cm^{-1} (C=O of cyclic five-membered ring anhydride); uv maxima (CH_3CN), 218 mμ (ϵ 6950), 273 (2230), and 280 (2060); nmr ($CDCl_3$), δ 6.6–7.4 (4 H multiplet, aryl CH), 4.24 (1 H, center of multiplet, benzylic CH), 3.75 (3 H singlet, CH_3O), and 3.17 (2 H, center of multiplet, $-CH_2CO-$).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.00; H, 4.97.

A more convenient preparation of the anhydride **9** consisted of melting 224 g (1.00 mol) of the diacid **8** under a nitrogen atmosphere in a flask fitted with a 30-cm Vigreux column and heated with an oil bath held at 220–240°. After the acid had melted, the pressure in the system was reduced to 0.2 mm and the acid–anhydride mixture was allowed to reflux for 30 min. A small amount of distillate was collected in a cold trap during this reflux period. After the reflux period was complete, the Vigreux column was removed and the residue was distilled in a short-path still (0.2 mm and 240° bath) to separate 200 g (97%) of the crude anhydride as a viscous liquid which solidified on standing. The combined distillates from four runs were dissolved in 700 ml of methylene chloride and allowed to stand for 5 hr during which time 24 g (2.7%) of unchanged diacid **8** (mp 176–177° dec) separated and was removed by filtration. The filtrate was diluted with methylene chloride to a volume of 1.3 l. and then 1 l. of ether and 1 l. of petroleum ether (bp 30–60°) were added to precipitate 720 g (87.5%) of the pure anhydride **9** as white prisms, mp 66.5–68°. An additional 24 g (2.9%) of anhydride **9** (mp 65–67°) was obtained from the mother liquors. The combined fractions collected in the cold trap, the mother liquors, and unchanged starting material after conversion of 2650 g (11.8 moles) of diacid **8** into 2175 g (89%) of anhydride **9** was reworked to obtain an additional 101 g of anhydride **9** (mp 66–67.5°), total yield 2276 g (93.1%).

Friedel–Crafts Cyclization of the Anhydride 9.—To a solution of 300 g (1.46 mol) of the anhydride **9** in 2.0 l. of methylene chloride was added, portionwise and with stirring, 405 g (3.04 mol) of $AlCl_3$ while the temperature of the reaction mixture was kept at 12–15° by means of a cooling bath. After the addition was complete, the cooling bath was removed and the mixture was stirred at room temperature for 2 hr. The reaction mixture was poured, with stirring, into a mixture of ice and 400 ml of concentrated, aqueous HCl and the crude organic product (*ca.* 300 g) was collected and allowed to dry. This crude acid was esterified by reaction with 6.0 l. of refluxing methanol containing 10 ml of concentrated H_2SO_4 for 16 hr. The reaction mixture was concentrated and a solution of the residual solid in chloroform was washed successively with aqueous 10% NaOH, water,

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(7) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. Unless otherwise stated, the ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. The chemical shift values are expressed either in cycles per second (cps) or δ values (ppm) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC, Model 21–130 or a Hitachi (Perkin–Elmer) mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(8) R. N. Icke, C. E. Redemann, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 564.

(9) C. F. H. Allen and F. W. Spangler, ref 8, p 377.

(10) D. H. Hey and K. A. Nagdy, *J. Chem. Soc.*, 1894 (1953).

(11) C. F. H. Allen and H. B. Johnson, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 804.

(12) Attempts to accomplish this hydrolysis with concentrated aqueous HCl as had been done with the analogous phenyl compound[11] led to poor yields of impure material, presumably because of concurrent cleavage of the methoxyl function.

(13) The toluene layer dissolved both the partially hydrolyzed material and colored by-products formed during the acidic hydrolysis. If toluene was not added, the diacid **8** initially isolated was impure (mp 168–174°) and relatively difficult to purify by crystallization.

and aqueous NaCl and then dried and concentrated. Recrystallization of the resulting solid from a benzene–cyclohexane mixture separated 215 g (67%) of the keto ester **11** as white needles: mp 116–117°; ir (CCl_4), 1720 (indanone C=O) and 1750 cm^{-1} (ester C=O); uv maxima, 223 mμ (ϵ 15,700), 268 (15,600), 285 (shoulder, 11,700), and 293 (shoulder, 9800); nmr ($CDCl_3$), δ 7.81 (1 H doublet, J = 9 cps, aryl CH at C-7), 6.8–7.5 (2 H multiplet, aryl CH), 4.0–4.5 (1 H multiplet, benzylic CH), 3.95 (3 H singlet, OCH_3), 3.83 (3 H singlet, OCH_3), and 3.02 (2 H, center of multiplet, $-CH_2CO-$).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49; mol wt, 220. Found: C, 65.31; H, 5.71; mol wt, 220 (mass spectrum).

To prove the substitution pattern in the aromatic ring of the keto ester **11**, a mixture of 1.0 g (4.5 mmol) of the keto ester **11**, 5.0 g of $KMnO_4$, 0.2 g of Na_2CO_3, and 50 ml of water was refluxed until the color of the permanganate was discharged. The resulting mixture was cooled, acidified, and extracted with ether. After the ethereal extract had been dried and concentrated, the residual solid was distilled in a short-path still (0.01 mm and 130° bath) and the distillate was recrystallized from a benzene–cyclohexane mixture to separate 75 mg of **4-methoxyphthalic anhydride** (**12**), mp 90–92°.[14] An authentic sample of this same anhydride **12** (identified by comparison of infrared spectra) was obtained by the comparable oxidation of 6-methoxy-1-indanone.

Concentration of the mother liquors remaining after crystallization of keto ester **11** afforded 22 g (7%) of a mixture[15] of the keto esters **11** and **10a**. A 4-g portion of this material was chromatographed on silicic acid to separate 1.25 g of keto ester **11** (in the early fractions eluted with hexane–ether mixtures) and 1.5 g of the keto ester **10a**, mp 93–96° (in the later fractions eluted with hexane–ether mixtures). Recrystallization from a benzene–cyclohexane mixture afforded 1.0 g of the pure **keto ester 10a** as white prisms: mp 95–96°; ir ($CHCl_3$), 1740 (ester C=O) and 1710 cm^{-1} (indanone C=O); uv maxima, 218 mμ (ϵ 25,800), 257 (10,400), and 312 (4800); nmr (CD_3COCD_3), δ 7.59 (1 H triplet, J = 8 cps, aryl CH at C-5), 7.17 (1 H doublet, J = 8 cps, aryl CH at C-4 or C-6), 6.96 (1 H doublet, J = 8 cps, aryl CH at C-4 or C-6), 4.1–4.5 (1 H multiplet, benzylic CH), 3.88 (3 H singlet, OCH_3), 3.72 (3 H singlet, OCH_3), 2.85 (2 H, center of multiplet, $-CH_2CO-$).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49; mol wt, 220. Found: C, 65.68; H, 5.56; mol wt, 220 (mass spectrum).

From a comparable Friedel–Crafts reaction, a small amount of the hydroxy keto ester **10b** was isolated from the base-soluble fraction. Recrystallization from a benzene–cyclohexane mixture afforded the pure **phenol 10b** as white needles: mp 88–89°; ir (CCl_4), 3330 (associated OH), 1750 (ester C=O), and 1690 cm^{-1} (indanone C=O lowered by intramolecular H bonding); uv maxima, 220 mμ (ϵ 22,800), 256 (10,300), and 315 (4140); nmr ($CDCl_3$), δ 9.25 (1 H singlet, OH), 6.8–7.8 (3 H multiplet, aryl CH), 4.0–4.6 (1 H multiplet, benzylic CH), 3.87 (3 H singlet, OCH_3), and 3.12 (2 H, center of multiplet, $-CH_2CO-$).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89; mol wt, 206. Found: C, 64.12; H, 5.00; mol wt, 206 (mass spectrum).

2,3-Dicarbomethoxy-5-methoxy-1-indanone (**13**).—To a vigorously stirred, warm (60°) suspension of 540 g (6.0 mol) of dimethyl carbonate, 65 g (2.7 mol) of sodium hydride [obtained by washing the dispersion in oil with petroleum ether (bp 30–60°)], 1 ml of methanol, and 100 ml of benzene was added a warm (*ca.* 70°) solution of 200 g (0.91 mol) of the keto ester **11** in 1000 ml benzene over a 100-min period. The rate of addition was adjusted such that the transient red color formed upon adding each drop of keto ester solution disappeared immediately and the reaction mixture remained a yellow-green color throughout the addition. After the addition was complete, the reaction mixture was maintained at 60° with stirring for 30 min and then cooled to 10° and acidified by the dropwise addition of 250 ml of acetic acid with stirring and external cooling. The reaction mixture was poured onto ice and the resulting mixture was acidified to pH 1 with aqueous HCl. After the organic layer had been separated, the aqueous phase was extracted with benzene and the combined organic layers were washed successively with water, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated. A solution of the residual brown oil (251 g) in 250 ml of methanol was cooled to −10° and the crystalline keto diester **13** which separated was collected and washed with 100 ml of cold (−50°) methanol and 300 ml of petroleum ether (bp 30–60°). The product **13** amounted to 228.5 g (90.5%) of light tan prisms, mp 60–64°. A sample, purified for analysis by crystallization from an ether–petroleum ether (bp 30–60°) mixture at −5°, melted at 58–60°. The variation in melting point of this product suggests that it probably a mixture of stereoisomers: ir (CCl_4), 1745 (ester C=O) and 1720 cm^{-1} (indanone C=O); uv maxima, 227 mμ (ϵ 13,100), 275 (15,100), 286 (14,500), and 296 (13,700); nmr ($CDCl_3$), δ 7.67 (1 H doublet, J = 8 cps, aryl CH at C-7), 6.8–7.3 (2 H multiplet, aryl CH at C-4 and C-6), 4.5–4.8 (1 H multiplet, benzylic CH), 4.0–4.3 (1 H multiplet, $COCHCO_2R$), 3.88 (3 H singlet, OCH_3), and 3.78 (3 H singlet, OCH_3).

Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.33; H, 5.19.

1,2-Dicarbomethoxy-6-methoxyindene (**4**).—A cold (0°) solution of 100 mg (0.36 mmol) of the keto diester **13** and 14 mg (0.39 mmol) of sodium borohydride in 10 ml of methanol was stirred at 0° for 1 hr and then the reaction mixture was acidified, concentrated, and partitioned between ether and aqueous $NaHCO_3$. The organic layer was dried and concentrated to leave 91 mg of oil which solidified on standing. Chromatography on silicic acid separated 56 mg of solid fractions eluted with hexane–ether mixtures. Repeated recrystallization from ether–petroleum ether (bp 30–60°) mixtures at −5° separated one stereoisomer of the hydroxy diester **14** as colorless prisms: mp 72.5–74°; ir (CCl_4), 3580, 3475 (unassociated and associated OH), and 1740 cm^{-1} (ester C=O); uv maxima, 227 mμ (ϵ 8560), 279 (2760), and 286 (2490); nmr ($CDCl_3$), δ 7.22 (1 H doublet, J = 9 cps, aryl CH at C-6 or C-7), 6.5–7.0 (2 H multiplet, aryl CH), 4.8–5.3 (1 H multiplet, >CHO–), 4.0–4.4 (1 H multiplet, benzylic CH), 3.1–3.5 (1 H multiplet, $>CHCO_2R$), 3.71, 3.74, and 3.77 (9 H, three singlets, OCH_3).

Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.75; H, 5.70.

For preparative purposes, it was more efficient to dehydrate the crude alcohol **14** without purification. To a cold (−35°) solution of 49.5 g (1.3 mol) of sodium borohydride in 2.0 l. of methanol (neutralized with Na_2CO_3 before use) was added, dropwise with stirring and external cooling under a nitrogen atmosphere, a solution of 260 g (0.935 mol) of the keto diester **13** in 1.0 l. of methanol. After the addition was complete (*ca.* 30 min), the yellow reaction mixture was stirred at −35° for 2 hr and then neutralized by the dropwise addition of 130 ml of acetic acid. The solution was concentrated under reduced pressure and the residual yellow semisolid was partitioned between water and benzene. The benzene solution was dried, mixed with 2.5 g of *p*-toluenesulfonic acid, and then refluxed under a nitrogen atmosphere for 1 hr with continuous separation of water. The resulting benzene solution was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated. A solution of the viscous yellow residue in a benzene–cyclohexane mixture deposited 198.9 g (81.3%) of the unsaturated diester **4** as pale yellow prisms, mp 97.5–99°. Recrystallization afforded an analytical sample as white needles: mp 97–98.5°; ir (CCl_4), 1740 (ester C=O) and 1720 cm^{-1} (conjugated ester C=O); uv maxima, 238 mμ (ϵ 10,600), 308 (14,700), and 318 (14,700); nmr ($CDCl_3$), δ 7.63 (1 H doublet, J = 2 cps, vinyl CH), 6.7–7.5 (3 H multiplet, aryl CH), 4.57 (1 H broad, benzylic CH), 3.78 (6 H singlet, OCH_3), and 3.67 (3 H singlet, OCH_3).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38; mol wt, 262. Found: C, 64.11; H, 5.18; mol wt, 262 (mass spectrum).

Preparation of the Indenedicarboxylic Acid Derivatives 19–22.—Following a modification of previously described directions,[3] a mixture of 5.76 g (0.24 mol) of sodium hydride, 19.0 g (0.13 mol) of diethyl oxalate, 50 ml of benzene, and 0.6 ml of ethanol was treated with a solution of 22.1 g (0.12 mol) of ethyl hydrocinnamate in 50 ml of benzene. When the reaction was complete, the mixture was neutralized by adding 5 ml of acetic acid and the crude keto diester **18a** was separated as 39 g of pale yellow oil. This crude ester **18a** was added, dropwise and with stirring, to 300 ml of cold (0–5°), concentrated H_2SO_4. After the resulting solution had been stirred at 0–5° for 2 hr, it was poured onto ice and then extracted with ether. The ethereal solution was washed successively with water, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated to leave 24 g of the crude

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[14] 4-Methoxyphthalic anhydride is reported to melt at 96°: R. Melby, R. Crawford, D. McGreer, and R. B. Sandin, *J. Amer. Chem. Soc.*, **78**, 3817 (1956). 3-Methoxyphthalic anhydride, the alternative possibility, is reported to melt at 159–160°: E. L. Schumann, M. G. Van Campen, and C. H. Tilford, *J. Org. Chem.*, **23**, 763 (1958).

[15] A thin layer chromatography plate coated with silicic acid and eluted with an ether–benzene mixture was employed for this analysis.

semisolid product. Recrystallization from a cyclohexane–petroleum ether (bp 30–60°) mixture afforded 16.05 g (51%) of the diester **19a** as pale yellow prisms: mp 75–77° (lit. mp 76–77°,[3a] 78° [3b]); ir (CCl_4), 1735 and 1715 cm^{-1} (coupled C=O vibrations of a diester); uv maxima, 229 mμ (ε 13,300), 236 (13,000), and 289 (15,300); nmr ($CDCl_3$), δ 7.2–7.7 (4 H multiplet, aryl CH), 4.44 and 4.29 (4 H, two overlapping quadruplets, each with J = 7 cps, ethoxy CH_2), 3.74 (2 H singlet, benzylic CH_2), and 1.41 and 1.33 (6 H, two overlapping triplets each with J = 7 cps, ethoxyl CH_3).

A mixture of 16.0 g (61 mmol) of the diester **19a** and 600 ml of aqueous 6 *M* HCl was heated under reflux for 4 hr and then mixed with ice, cooled, and filtered. The residual crude diacid **21** amounted to 15 g, mp 222–227° dec (lit. mp 215–217° dec,[3a] 215° dec[3b]). A portion of the material was recrystallized from aqueous ethanol to separate the diacid (presumably still a mixture **21**) as light tan needles, mp 236–238° dec. A suspension of 0.50 g of the crude diacid **21** (mp 222–227° dec) in 20 ml of ethyl acetate was esterified with excess ethereal diazomethane. The crude neutral product was isolated as 0.35 g of a yellow liquid which partially crystallized on standing. The crude product contained 90% of the diester **20** and 10% of the diester **19b** as determined by a subsequently described nmr analysis.

A suspension of 13 g (64 mmol) of this crude diacid **21** and 50 ml of acetic anhydride was heated to 110° with stirring for 1 hr. The resulting solution was cooled in an ice bath to separate 6.0 g of the crude anhydride **22** as orange needles, mp 150–165° dec. Recrystallization from benzene afforded the mixture of isomeric **anhydrides 22** as 4.2 g (36%) of orange needles, mp 150–170° dec.[16] Subsequent recrystallization and sublimation did not alter the melting behavior of this mixture; the infrared (CCl_4) bands were at 1845 and 1775 cm^{-1} (anhydride C=O in a five-membered ring).

Anal. Calcd for $C_{11}H_6O_3$: C, 70.97; H, 3.25. Found: C, 71.27; H, 3.40.

A 0.30-g sample of this anhydride mixture **22** was dissolved in 10 ml of boiling methanol and then the solution was concentrated under reduced pressure. A solution of the residual crude monomethyl ester in ethyl acetate was esterified with excess ethereal diazomethane. The nmr analysis of the resulting mixture of dimethyl esters (235 mg, mp 48–57°) indicated the presence of 66% of the diester **20** and 34% of the diester **19b**.

A solution of 7.0 g (34 mmol) of the crude diacid mixture **21** and 0.5 ml of concentrated H_2SO_4 in 350 ml of methanol was refluxed for 16 hr under a nitrogen atmosphere and then concentrated under reduced pressure. An ether solution of the residue was washed successively with water, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated to leave 3.9 g of crude diester as an oil which crystallized on standing, mp 52–57°. Recrystallization from a cyclohexane–petroleum ether (bp 30–60°) mixture afforded 3.16 g of a mixture of diesters as white prisms, mp 50–59°, which contained (nmr analysis) 87% of the diester **20** and 13% of the diester **19b**. Several fractional recrystallizations of this material from cyclohexane separated 0.28 g of the diester **20** as white needles: mp 59–61°; ir (CCl_4), 1745 (unconjugated ester C=O) and 1725 cm^{-1} (conjugated ester C=O); uv maxima, 228 mμ (ε 15,700), 236 (15,600), and 288 (15,700); nmr ($CDCl_3$), δ 7.1–7.8 (5 H multiplet, vinyl and aryl CH), 4.58 (1 H partially resolved multiplet, benzylic CH), 3.77 (3 H singlet, OCH_3) and 3.63 (3 H singlet, OCH_3).

Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21; mol wt, 232. Found: C, 67.07; H, 5.21; mol wt, 232 (mass spectrum).

Following previously described procedures, a mixture of 2.88 g (0.12 mol) of sodium hydride, 7.7 g (0.065 mol) of dimethyl oxalate, 0.3 ml of methanol and 25 ml of benzene was treated with a solution of 9.85 g (0.060 mol) of methyl hydrocinnamate in 25 ml of benzene. After the reaction was complete, the crude mixture was neutralized with 2.5 ml of acetic acid and the crude organic keto diester **18b** was isolated as 18 g of yellow oil. This keto diester **18b** was added dropwise and with stirring, to 150 ml of cold (0–5°), concentrated H_2SO_4. After the resulting solution had been stirred for 2 hr at 0–5°, it was poured onto ice and extracted with ether. The organic layer was washed successively with water, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated. The residual crude diester **19b** (6.1 g, mp 69–76°) was recrystallized from cyclohexane to separate the pure diester **19b** as 4.68 g (34%) of white prisms: mp 81–83°; ir (CCl_4), 1740 and 1720 cm^{-1} (coupled C=O vibrations of a diester); uv maxima, 228 mμ (ε 14,500), 236 (14,200), and 289 (15,400); nmr ($CDCl_3$), δ 7.2–7.7 (4 H multiplet, aryl CH), 3.96 (3 H singlet, OCH_3), 3.82 (3 H singlet, OCH_3), and 3.71 (2 H singlet, benzylic CH_2).

Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21; mol wt, 232. Found: C, 67.55; H, 5.43; mol wt, 232 (mass spectrum).

A series of known mixtures of diesters **20** and **19b** were prepared to establish the validity of an nmr analytical scheme based upon the areas under peaks δ 4.58 (from **20**) and 3.96 (from **19b**). To determine the equilibrium concentrations of the two esters, solutions of each of the diesters in 5–15 ml of methanol containing 20–25 mg of *p*-toluenesulfonic acid were refluxed for 60 hr and then concentrated. A solution of each residue in chloroform was washed successively with aqueous $NaHCO_3$ and aqueous NaCl, and then dried, concentrated, and analyzed by measuring its nmr spectrum. From 100 mg of the diester **20**, the recovered diesters (83 mg) contained 83% of **20** and 17% of **19b**. From 250 mg of the diester **19b**, the recovered diesters (240 mg) contained 87% of **20** and 13% of **19b**. Thus the average equilibrium concentration in refluxing methanol is 85% of diester **20** and 15% of diester **19b**.

A 0.50-g sample of a mixture of diesters containing (nmr analysis) *ca.* 5% of diester **19b** and *ca.* 95% of diester **20** was dissolved in 5 ml of cold (5°), concentrated H_2SO_4. After the solution had been stirred for 1 hr at 5°, it was poured onto ice and the resulting mixture was extracted with chloroform. The chloroform solution was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated. The residual oil (0.40 g), which crystallized on standing, contained (nmr analysis) *ca.* 95% of the diester **20** and *ca.* 5% of the diester **19b**.

1,2-Dicarbomethoxy-6-methoxy-1-indene (17).—Following previously described procedures, a mixture of 2.88 g (0.12 mol) of sodium hydride, 7.7 g (0.065 mol) of dimethyl oxalate, 0.2 ml of methanol, and 20 ml of benzene was treated with a solution of 11.6 g (0.060 mol) of methyl β-(*p*-methoxyphenyl)propionate (**15**) in 30 ml of benzene. The organic product (15 g or 89%) was a pale yellow oil. Although attempts to obtain analytically pure samples of the keto ester **16** were complicated by decarbonylation which accompanied distillation, a partially purified sample of the keto ester **16** was obtained as a pale yellow oil: $n^{27}D$ 1.5102, by distillation in a short-path still (0.1 mm and 150° bath); ir (CCl_4), 1760 (shoulder) and 1735 cm^{-1} (ester and ketone C=O); uv maxima, 226 mμ (ε 11,600), 277 (4480), and 283 (4140); nmr (CCl_4), δ 7.00 (2 H doublet, J = 9 cps, aryl CH), 6.66 (2 H doublet, J = 9 cps, aryl CH), 4.22 (1 H triplet, J = 7 cps, $COCHCO_2R$), 3.73 (3 H singlet, OCH_3), 3.67 (3 H singlet, OCH_3), 3.60 (3 H singlet, OCH_3), and 3.06 (2 H doublet, J = 7 cps, benzylic CH_2).

To 100 ml of cold (0–10°), concentrated sulfuric acid was added, dropwise and with stirring, 13 g (0.046 mol) of the crude keto diester **16**. The resulting solution was stirred for 2 hr at 5–10° and then poured onto ice and extracted repeatedly with chloroform. The organic extract was washed successively with aqueous NaOH and aqueous NaCl and then dried and concentrated. The residual pale yellow oil (1.7 g) contained[15] two components which could be detected under an ultraviolet lamp, the more rapidly eluted being the unsaturated ester **17**. Chromatography on silicic acid separated 75 mg of the crude diester **17** as a white solid, mp 105–110°, eluted in the early ether–hexane fractions and 480 mg of an unknown component (a pale yellow oil) eluted in the later hexane–ether fractions. The crude diester was recrystallized from cyclohexane to separate 40 mg of the pure diester **17** as white needles: mp 128–130°; ir ($CHCl_3$), 1735 and 1715 cm^{-1} (coupled C=O vibrations of a diester); uv maxima, 239 mμ (ε 11,500), 308 (13,600), and 318 (13,300); nmr ($CDCl_3$), δ 6.7–7.5 (3 H multiplet, aryl CH), 3.97 (3 H singlet, OCH_3), 3.83 (6 H singlet, two OCH_3), and 3.68 (2 H singlet, benzylic CH_2).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38; mol wt, 262. Found: C, 64.15; H, 5.58; mol wt, 262 (mass spectrum).

A solution of 34 mg of the diester **17** and 5 mg of *p*-toluenesulfonic acid in 5 ml of methanol was refluxed for 40 hr and then subjected to the usual isolation procedure. Recrystallization of the crude product from benzene afforded 10 mg of the diester **4**, mp 96–98°, identified with the previously described sample by a mixture melting point determination and comparison of infrared spectra.

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[16] Previous investigators (ref 3a) had recrystallized their crude anhydride from ethanol and described the product, mp 184–185°, as the anhydride solvated with one molecule of ethanol (ref 6).

To examine the equilibration of the unsaturated esters **4** and **17**, a solution of 250 mg of the diester **4** and 100 mg of *p*-toluenesulfonic acid in 5 ml of methanol-d_1 was refluxed for 56 hr and then concentrated. A chloroform solution of the residual solid was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated. Recrystallization of the residue from methanol gave 125 mg of the partially deuterated derivative of diester **4**, mp 97–98.5°. The nmr spectrum ($CDCl_3$) of this material corresponded to the spectrum described previously except that the doublet at δ 7.63 (vinyl CH) and the broad peak at 4.57 (benzylic CH) were of much diminished intensity. The mass spectrum of the material indicated the presence of 13% d_0 species, 54% d_1 species, and 33% d_2 species. In a similar experiment, a solution of 1.0 g of the diester **4** and 0.40 g of *p*-toluenesulfonic acid in 20 ml of methanol was refluxed for 48 hr and then subjected to the same isolation procedure. The pure recovered diester **4**, melting within the range 96–98°, amounted to 641 mg. The nmr spectrum of the crude solid (258 mg) recovered from the mother liquor indicated that less than 5% of the second unsaturated ester **17** was present as judged by the presence of only a very small nmr peak at δ 3.97 characteristic of one of the OCH_3 signals in the diester **17**. Accordingly, we conclude that less than 10% of the diester **17** is present in equilibrium with the diester **4**.

Reaction of the Unsaturated Anhydrides 22 with 1,3-Butadiene.—A solution of 3.55 g (1.88 mmol) of the anhydrides **22** (mixture of double-bond isomers as previously described), 0.50 g of diphenylsulfide (as an inhibitor), and 20 ml of liquid 1,3-butadiene in 50 ml of benzene was heated to 140° in an autoclave for 38 hr. The resulting mixture was concentrated under reduced pressure and a mixture of the residue with 75 ml of aqueous 10% NaOH was refluxed for 10 hr. The resulting aqueous solution was separated, washed with chloroform, acidified, and extracted with chloroform. The chloroform extract was washed successively with water and aqueous NaCl and then dried and concentrated to leave 2.18 g (45%) of the crude solid diacid **33a**. A small portion of this crude product was recrystallized from a methanol–cyclohexane mixture to separate the diacid **33a** as light tan needles, mp 148–152° dec. A 0.50-g portion of the crude diacid was distilled in a short-path still (0.1 mm and 190° bath) to separate the crude anhydride **34**. A cold (10°) cyclohexane solution of this crude product deposited 0.29 g of pure anhydride **34** as white prisms: mp 91–92.5°; ir (CCl_4), 1850 and 1790 (anhydride C=O in a five-membered ring); uv maxima (CH_3CN), 261 mμ (ϵ 903), 266 (1380), and 273 (1580); nmr ($CDCl_3$), δ 7.0–7.6 (4 H multiplet, aryl CH), 5.9–6.2 (2 H multiplet, vinyl CH), 3.71 and 3.19 (2 H, two doublets each with $J = 17$ cps, benzylic CH_2), and 2.0–3.2 (4 H multiplet, aliphatic CH).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; mol wt, 240. Found: C, 75.19; H, 5.09; mol wt, 240 (mass spectrum).

A solution of 0.50 of the crude diacid **33a** in 15 ml of ethyl acetate was esterified with excess ethereal diazomethane. The crude neutral product (0.30 g, mp 95–97°) was recrystallized from cyclohexane to separate the diester **33b** as light tan prisms: mp 95–97°; ir (CCl_4), 1745 cm^{-1} (ester C=O); uv maxima, 261 mμ (ϵ 805), 267 (1190), and 274 (1330); nmr ($CDCl_3$), δ 7.0–7.4 (4 H multiplet, aryl CH), 5.2–6.0 (2 H multiplet, vinyl CH), 3.73 (3 H singlet, OCH_3), 3.57 (3 H singlet, OCH_3), and 1.7–3.8 (6 H multiplet, aliphatic CH).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; mol wt, 286. Found: C, 71.11; H, 6.38; mol wt, 286 (mass spectrum).

Reaction of the Unsaturated Diester 4 with 1,3-Butadiene.—A mixture of 300 g (1.14 mol) of 2,3-dicarbomethoxy-5-methoxy-1-indene (**4**), 900 ml of benzene, 900 ml of liquid 1,3-butadiene, and 15 g of diphenylsulfide (added as an inhibitor) was heated to 190° in an autoclave under a helium atmosphere (400 psi) for 20 hr. The reaction vessel was cooled, an additional 900 ml of liquid 1,3-butadiene was added, and the resulting mixture was heated to 190° for 44 hr. The resulting yellow reaction mixture was concentrated under reduced pressure to leave a viscous yellow oil (850 g) which was vigorously extracted with ten 500-ml portions of boiling methanol to separate the methanol-soluble product from the insoluble polymeric material. The combined warm (45°) methanol extracts were filtered through Celite and then concentrated under reduced pressure. The residual yellow-green semisolid (350 g) was triturated with 350 ml of ether, allowed to stand at 0° for 2 days, and then filtered to separate the product (ether insoluble) from the solution of the remaining polymeric material. The residue was washed with 250 ml of cold (−70°) ether to leave 128 g (35.4%) of the diester **28a** as white prisms, mp 125–126°, which contained[15] only a minor amount of the starting unsaturated ester **4**. Recrystallization from methanol separated 117 g (32.4%) of the pure diester **28a** as white prisms: mp 126–127°; ir (CCl_4), 1735 cm^{-1} (ester C=O); uv maxima, 218 mμ (shoulder, ϵ 10,000), 284 (3180), and 292 (shoulder, 2840); nmr ($CDCl_3$), δ 6.5–7.3 (3 H multiplet, aryl CH), 5.6 (2 H broad, vinyl CH), 2.0–3.9 (6 H multiplet, aliphatic CH), 3.53, 3.68, and 3.75 (three 3 H singlets, OCH_3). Except for different numbers of methoxyl peaks the nmr spectra of esters **33b** and **28a** resemble one another closely in the region δ 2.0–4.0.

Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37; mol wt, 316. Found: C, 68.03; H, 6.25; mol wt, 316 (mass spectrum).

A mixture of 250 g (0.79 mol) of the diester **28a** and 190 g (4.75 mol) of NaOH in 1850 ml of methanol and 1700 ml of water was refluxed under a nitrogen atmosphere for 3 hr at which time 1.4 l. of methanol was allowed to distil from the mixture. The residual solution (bp 85°) was refluxed for an additional 20 hr and then concentrated under reduced pressure, diluted with water, and extracted with chloroform. The aqueous phase was filtered through Celite and then neutralized with aqueous HCl. The resulting solution was seeded with the diacid **28b** (to prevent the inital separation of the diacid as an oil) and then acidified to pH 1 by the dropwise addition of concentrated aqueous HCl. The mixture was cooled to 5° and the crude, crystalline diacid **28b** (232 g, mp 121–123° dec) was collected and washed with water. A 2.177-g sample of this crude diacid **28b** (contaminated with some sodium salt) was dissolved in methanol, acidified with aqueous HCl, and precipitated with added water to separate 2.08 g of the diacid **28b** as light tan prisms, mp 172–174° dec. A comparable sample of the diacid was crystallized from an ethyl acetate–petroleum ether (bp 30–60°) mixture to separate the diacid **28b** used for characterization as pale tan prisms: mp 165–167° dec; ir ($CHCl_3$), 1710 cm^{-1} (carboxyl C=O); uv maxima, 220 mμ (shoulder, ϵ 9430), 283 (3270), and 290 (2790).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.56.

When a 1.00-g sample of the crude diacid **28b** was heated to 180–200° at 0.2-mm pressure, the corresponding anhydride **29** distilled as 676 mg (72%) of colorless liquid. A solution of this distillate in a benzene–cyclohexane mixture deposited 485 mg of the pure anhydride **29** as white prisms: mp 78–80°; ir (CCl_4), 1850 and 1785 cm^{-1} (anhydride C=O in a five-membered ring); uv maxima (CH_3CN), 285 mμ (ϵ 3340) and 292 mμ (ϵ 3130); nmr ($CDCl_3$), δ 6.7–7.3 (3 H, multiplet, aryl CH), 5.8–6.1 (2 H multiplet, vinyl CH), 3.74 (3 H singlet, OCH_3), 2.8–3.7 (2 H, a partially resolved AB pattern, benzylic CH_2), and 2.0–3.1 (4 H multiplet, aliphatic CH). Except for the methoxy absorption the nmr spectra of the anhydrides **29** and **34** are practically identical in the region δ 2.0–4.0.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.03; H, 5.24.

To verify the relationship of the diester **28a** and the anhydride **29**, 300 mg of the anhydride was saponified with aqueous 10% NaOH and then acidified to yield 307 mg of the diacid **28b**, mp 167–170° dec. Esterification of this diacid **28b** with ethereal diazomethane gave, after recrystallization from a cyclohexane–petroleum ether (bp 30–60°) mixture, 190 mg of the diester **28a**, mp 124–125°, identified with the previously described sample by a mixture melting point determination.

A mixture of 1.00 g of the crude diacid **28b** and 0.50 g of a 30% palladium-on-carbon catalyst was heated to 235° over a 45-min period under a stream of nitrogen and then held at 235–240° for an additional 2 hr. The resulting mixture was cooled, partially dissolved in boiling benzene, and filtered through Celite. After the filtrate had been concentrated under reduced pressure, the residual solid (0.5 g) was chromatographed on silicic acid. The fractions eluted with an ether–hexane mixture (1:20 v/v) contained 0.40 g of 3-methoxyfluorene (**30**), mp 76–79°. Recrystallization from methanol afforded 0.31 g of the fluorene **30** as white needles: mp 78–80° (an additional recrystallization from cyclohexane raised the melting point to 82–83°); uv maxima, 259 mμ (ϵ 15,800), 268 (14,700), 305 (10,200), and 312 (11,600); uv maxima ($CHCl_3$), 263 mμ (ϵ 14,600), 271 (14,200), 306 (10,300), and 313 (11,600) [lit.[17] uv maxima ($CHCl_3$), 262 mμ (ϵ 20,000), 270 (20,000), 306

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[17] W. S. P. Neish, *J. Org. Chem.*, **16**, 694 (1951).

(13,000), and 312 (16,000)]; nmr (CDCl$_3$), δ 7.0–7.8 (6 H multiplet, aryl CH), 6.78 (1 H doublet of doublets, J = 2.5 and 8.5 cps, C-2 aryl CH), 3.77 (3 H singlet, OCH$_3$), and 3.69 (2 H singlet, benzylic CH$_2$); mass spectrum, molecular ion at *m/e* 196, abundant fragment peaks at *m/e* 181, 165, 153, and 152. The sample was identified with an authentic sample,[18] mp 76–78°,[19] by a mixture melting point determination and comparison of infrared spectra.

For comparison, a sample of 2-methoxyfluorene (**32**) was synthesized from the known[20] methoxyhexahydrofluorenone **31**. Wolff–Kisner reduction of 0.27 g of this ketone **31** with 0.6 g of KOH, 1.0 ml of aqueous 85% hydrazine, and 24 ml of diethylene glycol at 175–220° yielded 0.20 g of the crude hexahydrofluorene derivative which was mixed with 0.10 g of a 30% palladium-on-carbon catalyst and heated to 235° under a stream of nitrogen for 2.5 hr. The resulting mixture was extracted with chloroform and the resulting extract was filtered through Celite and concentrated under reduced pressure. The residual four-component mixture[21] (0.20 g, mp 95–99°) was chromatographed on silicic acid. The fractions (0.11 g, mp 97–101°, two components[21]) eluted with an ether–hexane (1:50 v/v) mixture were recrystallized from methanol to separate 30 mg of the pure 2-methoxyfluorene (**32**) as white needles: mp 107–108° (lit. mp 110–111°,[22a] 109° [22b,c]); uv maxima, 207 mμ (ϵ 35,500), 272 (22,100), 303 (6750), and 314 (6580); uv maxima (CHCl$_3$), 276 mμ (ϵ 19,400), 304 (7070), and 315 (6950) [lit.[23] uv maxima, 271 mμ (ϵ 22,000), 303 (6500), and 314 (6200); lit.[17] uv maxima (CHCl$_3$), 272 mμ (ϵ 20,000), 306 (6300), and 314 (6300)]; nmr (CDCl$_3$), δ 6.7–7.7 (7 H multiplet, aryl CH) and 3.74 (5 H singlet, OCH$_3$ and benzylic CH$_2$); mass spectrum, molecular ion at *m/e* 196, abundant fragment peaks at *m/e* 181, 153, and 152. The material was identified with a commercial sample[24] of the 2-methoxy isomer **32** by a mixture melting determination and comparison of infrared spectra. The spectra of the isomeric methoxyfluorenes **30** and **32** are distinctly different.

Registry No.—**4**, 15378-00-4; **6**, 6771-54-6; **7a**, 15378-01-5; **8**, 15378-02-6; **9**, 15378-03-7; **10a**, 15378-04-8; **10b**, 15378-05-9; **11**, 15378-06-0; **13**, 15378-07-1; **14**, 15378-08-2; **16**, 15378-09-3; **17**, 15378-10-6; **19b**, 15378-11-7; **20**, 15378-12-8; **21** (less highly substituted), 15378-13-9; **21** (more highly substituted), 15378-14-0; **22** (less highly substituted), 15378-15-1; **22** (more highly substituted), 5796-60-1; **28a**, 15412-43-8; **28b**, 15378-17-3; **29**, 15378-18-4; **33a**, 15378-19-5; **33b**, 15378-20-8; **34**, 15378-21-9.

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(18) This sample was purchased from K & K Laboratories, Inc., Plainview, N. Y.

(19) The compound has been reported to melt at (a) 84–85° [N. Ishikawa and M. Okuzaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 610 (1958); *Chem. Abstr.*, **53**, 3168 (1959)]; (b) 82–83° [W. S. P. Neish, *Rec. Trav. Chem.*, **69**, 207 (1950)]; and (c) 81–82° [W. D. Zahler and R. Huisgen, *Chem. Ber.*, **96**, 765 (1963)]. C. J. Collins and B. M. Benjamin [*J. Amer. Chem. Soc.*, **75**, 1644 (1953)] have reported the same compound to melt at 101–101.5°. This discrepancy may be attributable to the isolation of a second crystalline form of the 3-methoxyfluorene.

(20) W. G. Dauben and J. W. Collette [*ibid.*, **81**, 967 (1959)] report mp 99–100°. A sample, mp 98–99°, was prepared by Mr. T. M. Bare in our laboratories.

(21) A thin layer chromatography plate coated with silicic acid and eluted with a benzene–petroleum ether (bp 30–60°) mixture was employed for this analysis.

(22) (a) N. Ishikawa and M. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 467 (1958); *Chem. Abstr.*, **52**, 18340 (1958). (b) G. W. Gray, J. B. Hartley, and A. Ibbutson, *J. Chem. Soc.*, 2686 (1955). (c) J. D. Dickinson and C. Eaborn, *ibid.*, 2337 (1959).

(23) E. Sawicki, *J. Org. Chem.*, **21**, 271 (1956).

(24) Purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis.

Solvents of Low Nucleophilicity. X. Inductive and Participation Effects in the Addition of Trifluoroacetic Acid to Cyclopropanes[1]

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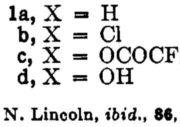
We have studied the carbonium ion formation which, formally, occurs in the ring-opening reactions of butylcyclopropane, 4-cyclopropyl-2-chlorobutane, and 4-cyclopropyl-2-butyl trifluoroacetate with trifluoroacetic acid. Cyclopropanes reacted approximately 300 times faster than comparable alkenes. Cyclopropane openings showed similar inductive effects but smaller effects of chlorine participation and (probably) hydrogen participation, compared with additions to unbranched alkenes and solvolyses of secondary tosylates.

Since quantitative information concerning the rates and products of electrophilic reactions of simple, substituted cyclopropanes is lacking, we have studied the reaction of trifluoroacetic acid with three substituted cyclopropanes carefully chosen to elucidate the role of hydrogen shifts and of inductive and participation effects in such reactions. The significance of the present study is that, by comparison with our previous studies, it provides the first comparison of carbonium ion formation *via* the following three different pathways: (1) cyclopropane opening, (2) additions to alkenes, and (3) tosylate solvolyses.

Increased interest in electrophilic ring-opening reactions of cyclopropanes has resulted from studies indicating the intermediacy of equilibrating edge- and/or end-protonated cyclopropane intermediates[2] and of the corresponding species derived from electrophilic attack of bromine[3] or acyl cations.[4] Although it is not yet known whether indications of unusual mechanisms will be confined to reactions of cyclopropane itself, the ring-opening reactions of substituted cyclopropanes take on new interest for comparison purposes. The presently reported study, however, has no direct connection with the question of unusual intermediates in reactions of cyclopropanes.

Description and Results

The compounds chosen for study were butylcyclopropane (**1a**), 4-cyclopropyl-2-chlorobutane (**1b**), and



1a, X = H
b, X = Cl
c, X = OCOCF$_3$
d, X = OH

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(2) R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964).

(3) N. C. Deno and D. N. Lincoln, *ibid.*, **86**, 252 (1964); **89**, 5357 (1966).

(4) H. Hart and R. L. Schlosberg, *ibid.*, **88**, 3347 (1966).