When k_{-5c} and k_{-5t} are very small relative to k_{6c} and k_{6t}, as the exchange data suggests they are for **9**, eq 2 further simplifies to eq 3.

$$\frac{d[cis]}{d[trans]} = \frac{k_{4c}k_{5c}k_{6c}(k_{-4t}k_{-5t} + k_{-4t}k_{6t} + k_{5t}k_{6t})}{k_{4t}k_{5t}k_{6t}(k_{-4c}k_{-5c} + k_{-4c}k_{6c} + k_{5c}k_{6c})} \quad (2)$$

$$\frac{d[cis]}{d[trans]} = \frac{k_{4c}k_{5c}(k_{-4t} + k_{5t})}{k_{4t}k_{5t}(k_{-4c} + k_{5c})} \quad (3)$$

Further, if $k_{5c} \cong k_{5t}$, as we have suggested above, and if $k_{-4c} \cong k_{-4t}$ or are small relative to k_5 and k_6 for **9**,[20] then eq 3 further simplifies to eq 4.

$$d[cis]/d[trans] = k_{4c}/k_{4t} \quad (4)$$

The product ratio from **9** is mostly a kinetic result, not a consequence of an equilibrium.

We have proposed the same to be true for hydrogenations at platinum surfaces, and suggest that the similarity of the results in Table VI for **9** are in support of our previous proposal.

Registry No.—Cyclohexene, 110-83-8; **2**, 591-49-1; **3**, 2808-76-6; **4**, 2808-79-9; **5**, 1759-64-4; **6**, 2808-77-7; **7**, 5502-88-5; **8**, 498-66-8; **9**, 14072-86-7; chlorodicyclooctenerhodium(I), 12112-71-9.

(20) The data tell us nothing about the magnitude of k_{-4} for **9**. However, the exchange studies show that k_{-4} [**14**] for **4–7** is smaller than k_5 [**14**] and that k_{-5} [**15**] (or the rate of the D_2–HD exchange step) is smaller than k_6 [**16**] particularly so for the intermediates leading to the more stable product isomer. The π complexes of **9** are much more stable than those of **4–7** (ref 14); hence these requirements for **9** are not unreasonable.

Perhydroindan Derivatives. XII.[1] 6-Methoxyindanone and Its Derivatives

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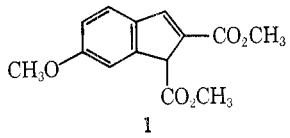
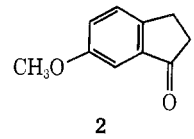
An optimum procedure for cyclizing *p*-methoxyhydrocinnamoyl chloride (**3b**) to 6-methoxyindanone (**2**) in 94% yield is described; the cyclization is conducted in dilute CH_2Cl_2 solution with no excess $AlCl_3$ present. When other procedures are employed, by-products resulting from solvent attack (**3c**) or intermolecular acylation (**5** and **6**) are produced and may become the major products. Several transformations of 1-indanone (**12**) and 6-methoxy-1-indanone (**2**) are described.

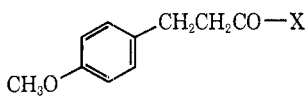
In seeking alternative routes to the indene diester **1**[2] and related compounds, the desirability of 6-methoxy-1-indanone (**2**) as an intermediate was apparent. Although a seemingly simple synthesis of this ketone **2** by an $AlCl_3$-catalyzed cyclization of the acid chloride **3b** had been reported,[3] at least three published attempts to repeat this cyclization have led to poor yields of the expected ketone **2**.[4] We have reinvestigated this cyclization in detail and describe here both a satisfactory method for forming the ketone **2** and the nature of the by-products when this cyclization is conducted under other than optimum conditions. We presume that the optimum conditions described for this cyclization will also be applicable to other Friedel–Crafts acylations *meta* to a methoxyl functions where difficulties have been noted.[3b]



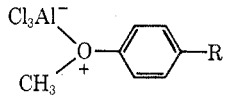
1



2



3a, X = OH
b, X = Cl
c, X = C_6H_5



4

In earlier work[4b] the *addition of the acid chloride to* a benzene solution containing excess $AlCl_3$ (1.7 equiv) (the procedure of ref 3) yielded a mixture of the indanone **2** (21%) and the phenyl ketone **3c** formed by attack of the acid chloride **3b**–$AlCl_3$ complex on the solvent. It seemed likely that these conditions (excess $AlCl_3$ throughout the reaction) served to deactivate the methoxyphenyl ring as a result of the excess $AlCl_3$ complexing with the methoxyl function (as in structure **4**).[5] Confirmation of this idea was readily obtained by the slow addition of an equimolar portion of $AlCl_3$ to a solution of the acid chloride **3b** in a relatively large volume of benzene. Under these circumstances the major product was the indanone **2** (90% yield) which was accompanied by only 8.3% phenyl ketone **3c**. Presumably, the formation of the indanone **2** in poor yield when the acid **3a** was added to excess polyphosphoric acid is also attributable to a similar deactivation by protonation of the methoxyl function. Seemingly, the above difficulties could be solved by following the normal Friedel–Crafts addition sequence in which only 1 equiv of $AlCl_3$ is added to a solution of the acid chloride in an inert solvent (*e.g.* CH_2Cl_2 rather than C_6H_6). However, when this procedure was followed, the crude indanone product **2** was accompanied by substantial amounts (15–40%) of a relative insoluble by-product from which we were able to separate the cyclic tetramer **5** (Scheme I) and a higher molecular weight polymer in

(1) This research has been supported by Public Health Service Grant 1-R01-CA-10933 from the National Cancer Institute and by Grant 68-1518 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

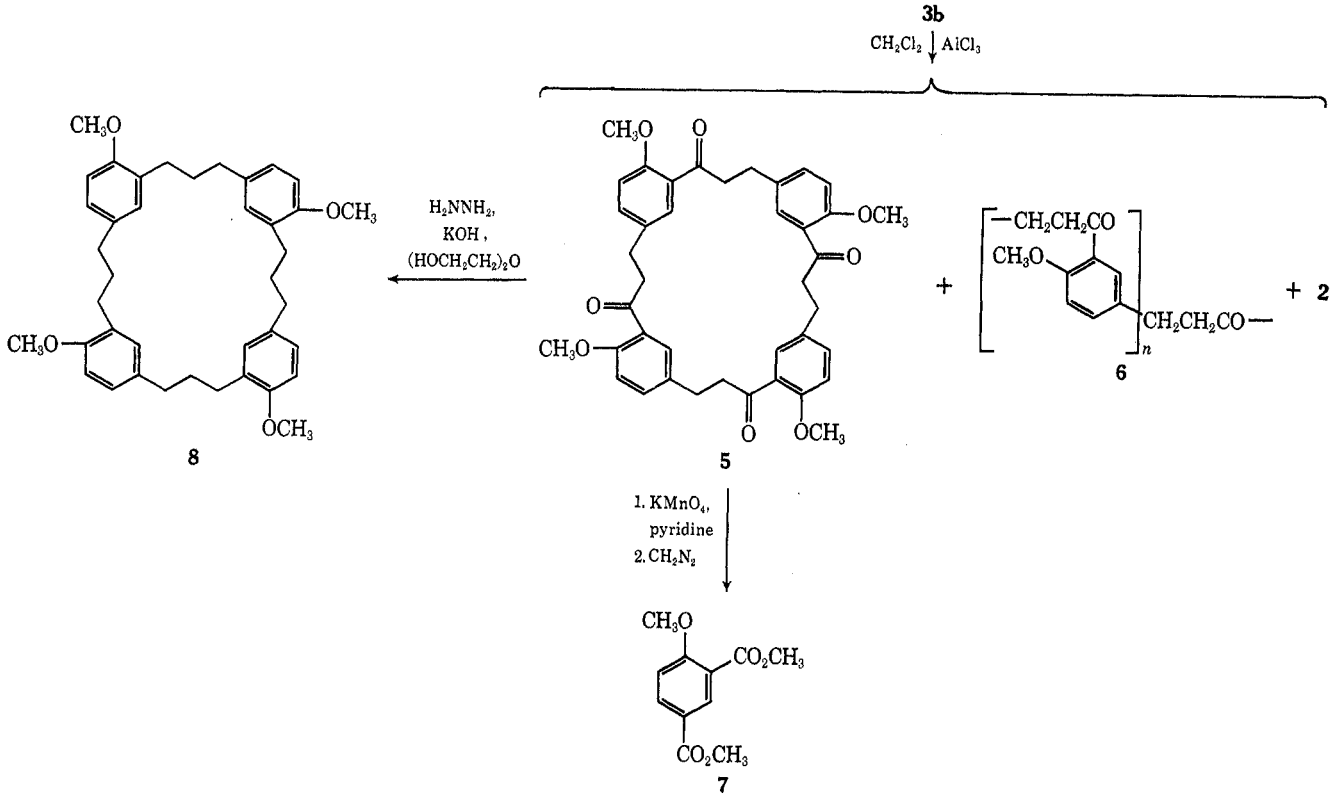
(2) H. O. House, J. K. Larson, and H. C. Müller, *J. Org. Chem.*, **33**, 961 (1968).

(3) (a) W. S. Johnson and W. E. Shelberg, *J. Amer. Chem. Soc.*, **67**, 1853 (1945); (b) W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949).

(4) (a) J. Sam and J. N. Plampin, *J. Amer. Chem. Soc.*, **82**, 5205 (1960); (b) H. O. House and J. K. Larson, *J. Org. Chem.*, **33**, 448 (1968); (c) R. V. Heinzelmann, H. G. Kolloff, and J. H. Hunter, *J. Amer. Chem. Soc.*, **70**, 1386 (1948).

(5) It is likely that the reaction is also complicated by cleavage of the ether when excess $AlCl_3$ is present.

SCHEME I

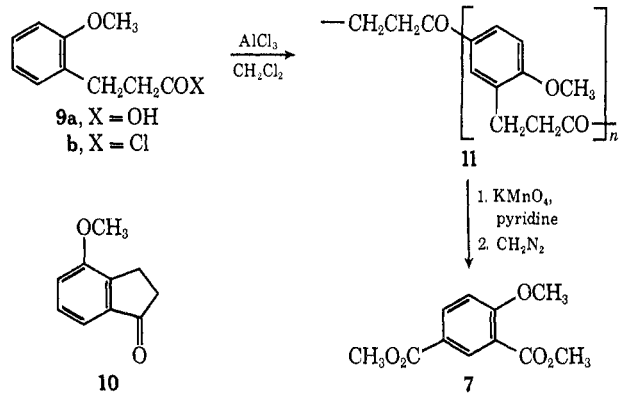


which the principal repeating unit is believed to be that illustrated in structure **6**. The substitution pattern in the tetrameric material was demonstrated both by spectroscopic data and by oxidative degradation to the diester **7**. Thus, even when deactivation of the methoxyphenyl ring by $AlCl_3$ was minimized, it was apparent that *intermolecular* acylation *ortho* to a methoxy function (to form **5** and **6**) was competitive in rate with *intramolecular* cyclization *meta* to the methoxyl group (to form **2**). Since the intermolecular reactions (to form **5** and **6**) are at least bimolecular processes, the competitive formation of the indanone **2** could obviously be enhanced by conducting the cyclization under conditions where the reactant (presumably the $AlCl_3$ complex of the acid chloride **3**) was at low concentration.[6] These reaction conditions, no excess $AlCl_3$ and a lower concentration of the acid chloride–$AlCl_3$ complex, were most conveniently achieved by the slow addition of equimolar quantities of the acid chloride **3b** and $AlCl_3$ to a relatively large volume of CH_2Cl_2. Under these conditions the yield of the methoxyindanone **2** was 94% and the formation of higher molecular weight by-products was negligible.

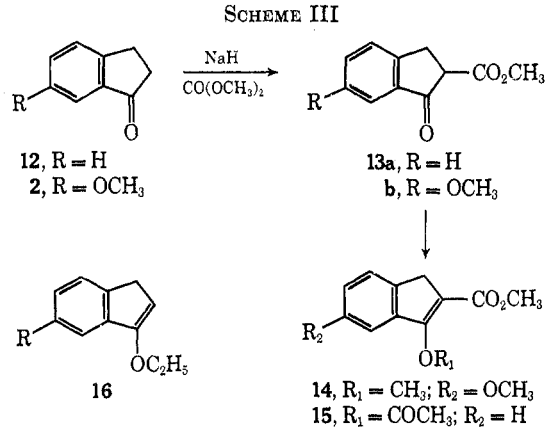
For the more recalcitrant case, cyclization of the acid chloride **9b** (Scheme II) to 4-methoxy-1-indanone (**10**),[4c,7] even the procedure developed for obtaining optimum yields in the cyclization **3b** → **2** failed. Only a higher molecular weight product believed to have the repeating unit **11** was isolated. As before, oxidative degradation yielded the diester **7**.

The indanones **2** and **12** (Scheme III) were converted into the indicated derivatives **13**, **14**, and **15** to learn if methods could be found to replace the C-3 methoxyl or acetoxyl functions of **14** or **15** by a cyano group. Since reaction of the enol ether **14** with HCN, a reaction which succeeded with a related hexahydrofluo-

SCHEME II



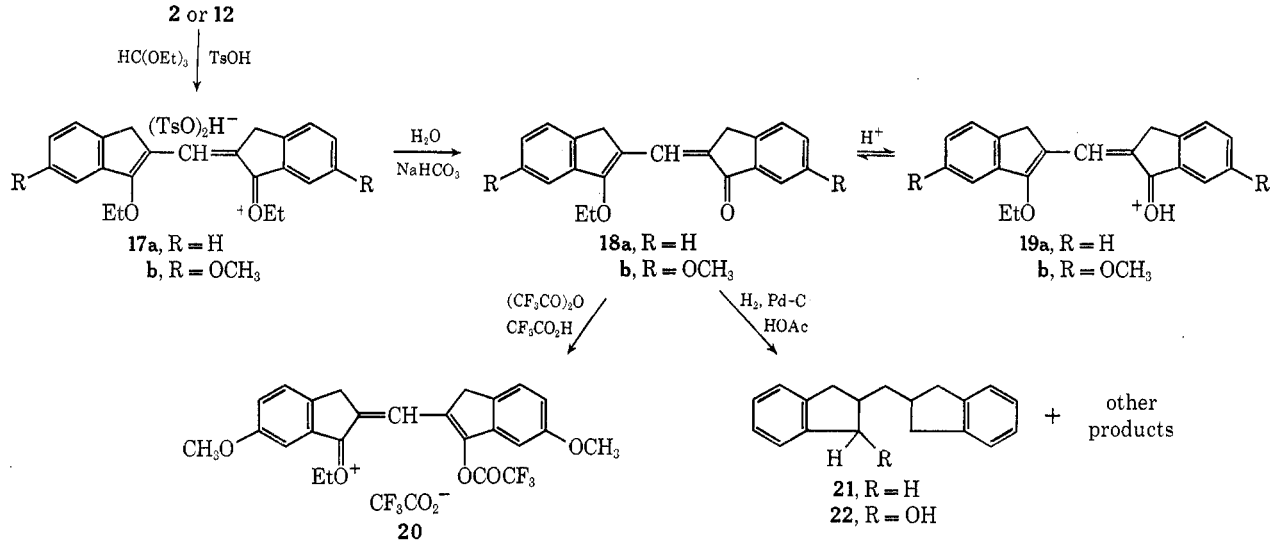
SCHEME III



(6) The product ketone **2** is apparently inert to further acylation.

(7) (a) K. V. Levshina and I. I. Kolodkina, *J. Gen. Chem. USSR*, **30**, 3656 (1960); (b) R. A. Barnes, E. R. Kraft, and L. Gordon, *J. Amer. Chem. Soc.*, **71**, 3523 (1949).

SCHEME IV



renone derivative,[8] was not successful, we sought to prepare the less highly substituted enol ether **16** by reaction of the indanones with ethyl orthoformate and *p*-TsOH. However the major product from these reactions proved to be the deeply colored oxonium salts **17** (Scheme IV), apparently derived from rapid reaction of the initially formed enol or enol ethers **16** with ethyl formate or ethyl orthoformate. The structures of the salts and neutral condensation products **17–20** were deduced from the spectroscopic properties of these substances, and the carbon skeleton of the unsubstituted series (**17a**, etc.) was proved by hydrogenation of **18a** to yield products **21** and **22**.

Experimental Section[9]

Cyclization of the Acid Chloride 3b. A. Dilute Solution in CH_2Cl_2.—Samples of the acid chloride **3b** (63.5 g, 0.32 mol) and $AlCl_3$ (46.0 g, 0.345 mol) were each divided into four equivalent portions and these portions were added at 1-hr intervals to 1.5 l. of cold (5°) CH_2Cl_2. After the final addition, the orange-red solution was stirred for 1 hr at 25°, poured into ice–water, and extracted with Et_2O. After the Et_2O extract had been washed with H_2O, aqueous NaOH, and aqueous NaCl, it was dried and concentrated. Recrystallization of the residual solid from hexane afforded 48.9 g (94%) of the indanone **2** as crops of pale tan needles, mp 107.5–109.5° (lit.[5] mp 108–108.5°,[3] 108–109°[4b]). A similar cyclization in dilute solution was achieved by the addition, portionwise with stirring over 15 min, of 2.80 g (21 mmol) of $AlCl_3$ to a solution of 3.92 g (19.7 mmol) of the acid chloride **3b** in 500 ml of CH_2Cl_2. After the resulting solution had been stirred at 25° for 2 hr, the same isolation procedure separated 2.87 g of indanone **2**, mp 109–110°, and 0.17 g of less pure product, mp 105–108°, total yield 3.04 g (95%).

B. Dilute Solution in PhH.—A solution of 5.00 g (25 mmol) of the acid chloride **3b** in 500 ml of PhH was treated with 3.50 g (26 mmol) of $AlCl_3$ and the resulting solution was stirred at 25° for 1 hr. After the usual isolation procedure had been followed, 3.08 g of the indanone **2**, mp 107.5–109°, was separated by crystallization from hexane. Chromatography (silica gel)[4b] separated 520 mg of the crude phenyl ketone **3c**, which crystallized from pentane as 497 mg (8.3%) of white needles, mp 62–63° (lit.[4b] mp 62–63°). The later chromatography fractions afforded an additional 580 mg of the indanone **2**, mp 107–109°, total yield 3.66 g (90%). Acidification of the aqueous alkaline washes afforded 21 mg of the acid **3a**, mp 100–102° (lit.[4b] mp 103.5–104°).

C. In CH_2Cl_2 at Typical Concentrations.—To a solution of 59 g (0.30 mol) of the acid chloride **3b** in 850 ml of CH_2Cl_2 at 12–15° was added, portionwise with stirring over 15 min, 42.5 g (0.32 mol) of $AlCl_3$. A yellow-orange complex separated from solution as the $AlCl_3$ was added. The resulting solution was stirred at 25° for 45 min and then poured into ice–water. The resulting mixture was filtered through Celite to remove the polymeric materials which were insoluble in either CH_2Cl_2 or H_2O. The CH_2Cl_2 phase of the filtrate was separated and the aqueous layer was extracted with $CHCl_3$. After the combined organic solutions had been dried and concentrated, the residual solid was extracted repeatedly with boiling hexane. When cooled, the hexane extracts deposited a total of 33.0 g (68%) of fractions of the indanone **2**, mp 107–109°. The hexane-insoluble material was recrystallized from $CHCl_3$ to separate 2.77 g (*ca.* 5%) of the solvate of the tetramer **5** as colorless prisms, mp 191–192°. This material crystallized from PhH as colorless prisms of a PhH solvate which lost the solvent when heated above 100°: mp 191–192°; ir ($CHCl_3$) 1680 cm^{-1} (conjugated C=O); uv (95% EtOH) 215 mμ (ε 30,700), 247 (13,000), and 310 (6120); nmr [$(CD_3)_2SO$] δ 6.8–7.2 (m, 12 H, aryl CH), 3.72 (s, 12 H, OCH_3), and 2.6–3.2 (m, 16 H, aliphatic CH).

Anal. Calcd for $C_{40}H_{40}O_8$: C, 74.05; H, 6.22; mol wt, 648. Found: C, 73.95; H, 6.21; mol wt, 648[10] (mass spectrum).

In a comparable reaction where 9.0 g (45 mmol) of the acid chloride **3b** and 6.65 g (50 mmol) of $AlCl_3$ in 200 ml of CH_2Cl_2 were employed, the total yield of the indanone **2** was 4.86 g (55%) and the yield of the solvate of the tetramer **5** was 219 mg (*ca.* 2.5%). The insoluble polymeric fraction amounted to 1.07 g (*ca.* 15%).[11] From the aqueous phases, 398 mg (5%) of the acid **3a** was recovered along with 590 mg of a weakly acidic liquid product which we presume to be a mixture of phenols.

A solution of 1.00 g (1.55 mmol) of the tetraketone **5**, 2.0 g of KOH, and 3.5 ml of 85% H_2NNH_2 in 30 ml of $(HOCH_2CH_2)_2O$ was refluxed for 3 hr and then heated to 190–200° for 4 hr. The resulting mixture was cooled, poured into cold aqueous HCl, and extracted successively with $CHCl_3$ and EtOAc. After the combined extracts had been washed with aqueous NaCl, dried, and concentrated, a solution of the residual solid in 30 ml of acetone was treated successively with 6.4 g of KOH in 22 ml of

(8) W. E. Parham and L. J. Czuba, *J. Amer. Chem. Soc.*, **90**, 4030 (1968).

(9) 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. The ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer. The nmr spectra were determined at 60 MHz with a Varian Model A-60 or T-60 nmr spectrometer. The chemical-shift values are expressed either in cycles per second or δ values (parts per million) relative to tetramethylsilane as internal standard. The mass spectra were obtained with a Perkin-Elmer Hitachi mass spectrometer. Unless otherwise states, all reactions involving strong bases, metals, or organometallic reagents were performed under a nitrogen atmosphere.

(10) We are indebted to Professor A. V. Robertson, Department of Organic Chemistry, University of Sydney, for determining the mass spectrum with a AEI Model MS-9 mass spectrometer.

(11) When more concentrated solutions of the reactants were employed, the yield of this insoluble fraction was as high as 40%.

H_2O and 10 ml of Me_2SO_4 in 8 ml of acetone to methylate any phenolic groups present. After the mixture had been stirred at 60° for 30 min and then at 95° for 1 hr, it was cooled and 920 mg of the tetraether **8**, which separated as a white solid, was collected. Chromatography (silica gel) separated the pure tetraether **8** in fractions eluted with $CHCl_3$. The ether **8** crystallized from PhH as colorless needles of a PhH solvate which lost the solvent when heated to 100° under reduced pressure: mp 203–204°; yield 815 mg (89%); ir ($CHCl_3$) no OH or C=O absorption in the 3- or 6-μ region; nmr ($CDCl_3$) δ 6.6–7.2 (m, 12 H, aryl CH), 3.73 (s, 12 H, OCH_3), 2.4–2.8 (m, 16 H, benzylic CH_2), and 1.6–2.1 (m, 8 H, aliphatic CH).

Anal. Calcd for $C_{40}H_{48}O_4$: C, 81.04; H, 8.16; mol wt, 592. Found: C, 81.32; H, 8.21; mol wt, 592[10] (mass spectrum).

A solution of 3.0 g of $KMnO_4$ in 25 ml of H_2O was added, dropwise and with stirring over 4 hr, to a warm (90–95°) mixture of 356 mg (0.55 mmol) of the tetraketone **5**, 25 ml of aqueous 0.2 *M* NaOH, and 50 ml of pyridine. The mixture was heated with stirring for an additional 3 hr and then the excess oxidant was consumed with $NaHSO_3$ and the mixture was filtered. The colorless filtrate was concentrated, acidified, and continuously extracted with Et_2O for 24 hr. After the Et_2O extract had been concentrated, the residual solid was esterified with excess ethereal CH_2N_2. The resulting neutral product was crystallized from hexane to separate 349 mg (71%) of dimethyl 4-methoxybenzene-1,3-dicarboxylate (**7**) as white needles: mp 95–95.5° (lit.[12] mp 94°); ir (CCl_4) 1725 cm^{-1} (conjugated ester C=O); nmr ($CDCl_3$) δ 8.51 (d, 1 H, J = 2.2 Hz, aryl C_2 H), 8.17 (d of d, 1 H, J = 2.2 and 8.8 Hz, aryl C_6 H), 7.06 (d, 1 H, J = 8.8 Hz, aryl C_5H), 3.97 (s, 3 H, OCH_3), and 3.92 (s, 6 H, OCH_3).

D. Reaction of the Acid 3a with Polyphosphoric Acid.—A solution of 3.0 g (16.7 mmol) of the acid **3a** in 65 g of polyphosphoric acid was heated to 60° for 1 hr, poured into ice–water, and extracted with EtOAc. The insoluble polymer (1.74 g, *ca.* 65%) was removed by filtration and the organic solution was dried and concentrated. The previously described extraction and crystallization procedures separated 329 mg (12%) of the indanone **2**, mp 105–107°, and 41 mg (1.5%) of the tetramer **5**, mp 190–191°, identified with the previously described sample by comparison of ir spectra. Part of the starting acid (156 mg, 5%) was also recovered.

Attempted Cyclization of the Acid Chloride 9b.—*o*-Methoxycinnamic acid,[13] mp 188–189°, was hydrogenated at 27° (1 atm) in EtOH over a Raney Ni catalyst to yield the saturated acid **9a**, mp 89–90° (lit. mp 83–84°,[14a] 87–89°[14b]), which was converted into the acid chloride **9b** with $SOCl_2$ in the usual way. The acid chloride **9b** was collected as a colorless liquid: bp 83–85° (0.1 mm); ir (CCl_4) 1805 cm^{-1} (COCl); nmr (CCl_4) δ 6.6–7.3 (m, 4 H, aryl CH), 3.72 (s, 3 H, OCH_3) and 2.7–3.3 (m, 4 H, aliphatic CH). To a cool (10°) solution of 3.15 g (15.9 mmol) of the acid chloride **9b** in 400 ml of CH_2Cl_2 was added, portionwise and with stirring over 10 min, 2.20 g (16.5 mmol) of $AlCl_3$. After the mixture had been stirred at 26° for 1.5 hr and then poured into ice–water, the CH_2Cl_2-insoluble polymer (2.198 g) was separated by filtration. The CH_2Cl_2 solution was washed with aqueous Na_2CO_3 and aqueous NaCl and then dried and concentrated to leave 392 mg of amorphous solid. The total solid (2.59 g, *ca.* 100%) exhibited no definite melting point. A 819-mg (5.05 mmol) portion of the product was suspended in 30 ml of pyridine and treated successively with 0.5 g of NaOH in 10 ml of H_2O and 3.0 g of $KMnO_4$ in 20 ml of H_2O. After the mixture had been heated to 90–95° for 6 hr, an additional 2.0 g of $KMnO_4$ in 15 ml of H_2O was added and heating was continued for 5 hr. The previously described isolation and esterification procedures were followed, and 737 mg (65%) of the diester **7**, mp 94–95.5°, was obtained.

Dimethyl 3-(4-Methoxybenzyl)-2-ketosuccinate.—The crude α-keto ester, prepared from 19.4 g (0.10 mol) of methyl 3-(4-methoxyphenyl)propionate and excess $(CO_2Me)_2$ as described earlier,[2] was treated with 15.0 g (75 mmol) of $Cu(OAc)_2$ in 150 ml of H_2O to yield, after 3 hr at 25°, 31.2 g of the crude Cu(II) complex, mp 183–185° dec. Recrystallization from benzene gave 23.28 g (75%) of the pure copper complex as green needles: mp 191–193° dec; ir ($CHCl_3$) 1745 (ester C=O) and 1615 and 1515 cm^{-1} (enolate of β-keto ester).

A 5.0-g sample of this Cu(II) complex was partitioned between aqueous 1.5 *M* H_2SO_4 and Et_2O and the Et_2O layer was washed with aqueous NaCl and concentrated. The crude enol form of the keto diester which remained [4.1 g (92%), mp 45–48°] was recrystallized from MeOH to separate one of the stereoisomers of the pure enol form as colorless needles: mp 50–52°; ir (CCl_4) 1745 (ester C=O) and 1665 and 1515 cm^{-1} (enolic β-keto ester); nmr (CCl_4) δ 12.40 (s, 1 H, OH), 7.05 (d, 2 H, J = 9 Hz, aryl CH), and 6.70 (d, 2 H, J = 9 Hz, aryl CH), with a series of overlapping peaks at δ 3.79 (s, OCH_3), 3.70 (s, OCH_3), 3.69 (s, OCH_3), and 3.6–3.8 (m, benzylic CH_2).

Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.99; H, 5.86.

As in earlier studies,[2] a variety of efforts to cyclize this α-keto diester to the olefinic diester **1** with PPA, H_2SO_4, or $AlCl_3$ lead to only very poor yields of the desired diester **1**.

Preparation of the β-Keto Esters 13. A. From 6-Methoxy-1-indanone (2).—To a warm (60°) suspension of 6.0 g (0.25 mol) of NaH and 54.0 g (0.60 mol) of $(MeO)_2CO$ in 150 ml of PhH was added, dropwise and with stirring over 1.75 hr, a solution of 16.2 g (0.10 mol) of the ketone **2** in 150 ml of PhH. After the mixture had been stirred at 60° for 30 min, it was cooled to 0°, acidified with 25.0 g (0.415 mol) of HOAc, and poured into an ice–HCl mixture. The combined organic layer and PhH extract of the aqueous phase were washed successively with aqueous $NaHCO_3$ and aqueous NaCl, dried, and concentrated. Recrystallization of the residue from hexane gave 21.1 g (96%) of the keto ester **13b**, mp 75–78°. Recrystallization gave the pure keto ester **13b** as colorless needles: mp 79–79.5°; ir (CCl_4) 1750 (ester C=O), 1720 (ketone and conjugated ester C=O), and 1660 cm^{-1} (enol C=C); uv (95% EtOH) 218 mμ (ϵ 23,400), 251 (9500), and 322 (5500); nmr ($CDCl_3$) δ 7.1–7.6 (m, 3 H, aryl CH), 3.84 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), and 3.3–4.2 (m, 3 H, aliphatic CH); mass spectrum *m/e* (rel intensity) 220 (26, M^+), 162 (38), 161 (40), 160 (100), 134 (52), 119 (20), 91 (31), 89 (30), 63 (32), 51 (20), and 44 (58).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.42; H, 5.57.

Reaction of 2.72 g (12.4 mmol) of the partially enolic β-keto ester **13b** with excess ethereal CH_2N_2 at 0° for 24 hr and 25° for 1 hr yielded 2.84 g (98%) of the crude enol ether **14** as colorless plates from pentane, mp 50–53°. Recrystallization afforded the pure enol ether **14**: mp 49.5–51°; ir (CCl_4) 1710 cm^{-1} (conjugated ester C=O); uv 95% EtOH) 222 mμ (ϵ 16,700), 285 (14,000), and 313 (9850); nmr (CCl_4) δ 6.7–7.3 (m, 3 H, aryl CH), 4.26 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), and 3.43 (s, 2 H, benzylic CH_2); mass spectrum *m/e* (rel intensity) 234 (51, M^+), 175 (100), and 160 (45).

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.55; H, 5.92.

B. From 1-Indanone (12).—The same procedure was applied to 23.80 g (0.18 mmol) of 1-indanone (**12**), 10.8 g (0.45 mol) of NaH, and 90.0 g (1.00 mol) of $(MeO)_2CO$ in 150 ml of PhH. The crude product (an orange oil) was distilled to separate 31.2 g (91%) of the β-keto ester **13a**, bp 109–111° (0.1 mm), which solidified on standing, mp 49–55°. Recrystallization from hexane gave the keto ester **13a** as colorless prisms (apparently a mixture of keto and enol forms): mp 51–60°; ir (CCl_4) 1750 (ester C=O), 1725 (keto and conjugated ester C=O), and 1665 cm^{-1} (enol C=C); uv (95% EtOH) 247 mμ (ϵ 11,300) and 294 (5850); nmr (CCl_4) δ 10.3 (br s, *ca.* 0.1 H, enolic OH), 7.2–7.8 (m, 4 H, aryl CH), 3.73 (s, 3 H, OCH_3), and 3.2–3.8 (m, *ca.* 3 H, aliphatic CH); mass spectrum *m/e* (rel intensity) 190 (15, M^+), 131 (52), 130 (100), 103 (61), 102 (61), 77 (20), 76 (32), 75 (24), 74 (20), 63 (21), 51 (47), and 50 (33).

Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.69; H, 5.36.

A mixture of 3.80 g (20 mmol) of the keto ester **13a**, 90 mg of TsOH, and 20 ml of isopropenyl acetate was refluxed for 3 hr, during which time 6 ml of distillate containing acetone was removed from the mixture. The resulting mixture, from which some of the crystalline product **15** separated, was partitioned between Et_2O and aqueous $NaHCO_3$. The crystalline product which remained was separated and the Et_2O layer was washed with aqueous NaCl, dried, and concentrated. The combined organic products were crystallized from PhH–hexane to separate 3.96 g (86%) of the enol acetate **15** as colorless needles: mp 142–143° (recrystallization raised the melting point to 143–143.5°); ir ($CHCl_3$) 1785 (enol ester C=O) and 1705 cm^{-1} (conjugated ester C=O); uv (95% EtOH) 227 mμ (ϵ 10,300), 234 (9050),

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(14) (a) R. Pschorr and H. Einbeck, *Ber.*, **38**, 2067 (1905); (b) K. v. Auwers, *Justus Liebigs Ann. Chem.*, **415**, 159 (1918).

and 285 (18,500); nmr ($CDCl_3$) δ 7.2–7.5 (m, 4 H, aryl CH), 3.47 (s, 3 H, OCH_3), 3.38 (s, 2 H, benzylic CH_2), and 2.37 (s, 3 H, $COCH_3$); mass spectrum *m/e* (rel intensity) 232 (1, M^+), 192 (9), 131 (25), 130 (100), 103 (28), 102 (94), 101 (33), 77 (35), 76 (38), 75 (39), 74 (26), 63 (24), 51 (35), 50 (31), and 43 (43).

Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.48; H, 5.24.

Reaction of the Indanones with Triethyl Orthoformate. A. 1-Indanone (12).—When solutions of 860 mg (6.52 mmol) of 1-indanone (**12**) in 5 ml of $(EtO)_3CH$ and 1.24 g (6.52 mmol) of TsOH in 5 ml of $(EtO)_3CH$ were mixed, a deep red color developed immediately and golden yellow crystals separated within a few minutes. After the mixture had stood for 10 min at 25–30°, the crystalline product was collected and washed successively with $(EtO)_3CH$–hexane (3:5, v/v) and hexane to leave 1.806 g (82%) of the salt **17a** as golden prisms, mp 116–118°. Recrystallization of the salt from CH_2Cl_2–hexane gave 1.278 g of the hydroscopic salt **17a**: mp 120–121°; ir (CH_2Cl_2) no C=O absorption in the 6-μ region; nmr [10% $(CF_3CO)_2O$ in CF_3CO_2H] δ 8.8 (br s, 1 H, vinyl CH), 7.1–8.2 (m, 16 H, aryl CH), 5.12 (q, 4 H, J = 7 Hz, ethoxyl CH_2), 3.94 (s, 4 H, aliphatic CH), 2.34 and 2.45 [2 s, 6 H, aryl CH_3 of $(TsO)_2^-H$], and 1.72 (t, 6 H, J = 7 Hz, ethoxyl CH_3).

Anal. Calcd for $C_{37}H_{38}O_8S_2$: S, 9.50. Found: S, 9.41.

When the salt **17a** (3.78 g, 5.6 mmol) was stirred with a cold (0°) mixture of 50 ml of aqueous $NaHCO_3$, 20 ml of EtOH, and 50 ml of Et_2O, the deep red color immediately changed to yellow. The Et_2O layer and Et_2O extract of the aqueous phase were combined, washed with aqueous NaCl, dried, and concentrated. Recrystallization (EtOH) of the residual yellow solid afforded 1.578 g (93.5%) of the ketone **18a** as pale orange needles, mp 124–125°, which melted at 125–126° after an additional recrystallization from EtOH–hexane: ir (CCl_4) 1695 (conjugated C=O in a five-membered ring) and 1620 cm^{-1} (C=C); uv (95% EtOH) 267 mμ (ε 10,400) and 406 (33,600). After a solution in CH_2Cl_2 was treated with several equivalents of CF_3CO_2H to generate the salt **19a**, the spectrum had maxima at 510 mμ (ε 43,000), 524 (44,000), and 546 (89,500); nmr ($CDCl_3$) δ 7.0–8.0 (m, 9 H, aryl and vinyl CH), 4.25 (q, 2 H, J = 7 Hz, ethoxyl CH_2), 3.55 (s, 2 H, benzylic CH_2), 3.40 (s 2 H, benzylic CH_2), and 1.35 (t, 3 H, J = 7 Hz, ethoxyl CH_3).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.48; H, 6.11.

The same ketone **18a** could be obtained directly from the reaction of the indanone **12**, $(EtO)_3CH$, and TsOH in 77% yield if the reaction mixture was worked up by the successive addition of EtOH and aqueous $NaHCO_3$.

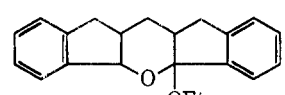
B. 6-Methoxy-1-indanone (2).—The analogous reaction of 1.62 g (10 mmol) of the indanone **2**, 1.90 g (10 mmol) of TsOH, and 15 ml of $(EtO)_3CH$ afforded a deep red-purple solution from which the salt **17b** separated and was collected. The salt was recrystallized from CH_2Cl_2 to give 1.611 g (44%) of the salt **17b** as golden needles: mp 100–101°; nmr [10% $(CF_3CO)_2O$ in CF_3CO_2H] δ 8.80 (s, 1 H, vinyl CH), 7.1–8.1 (m, 14 H, aryl CH), 5.10 (q, 4 H, J = 7 Hz, ethoxyl CH_2), 3.93 (s, 6 H, OCH_3), 3.90 (s, 4 H, benzylic CH_2), 2.35 and 2.45 [2 s, 6 H, aryl CH_3 of $(TsO)_2^-H$], and 1.70 (t, 6 H, ethoxyl CH_3). The mother liquors from these crystallizations were partitioned between $CHCl_3$ and aqueous Na_2CO_3 and the pale orange organic layer was washed with aqueous NaCl, dried, and concentrated.

Recrystallization (EtOH) of the residue afforded 708 mg (39%) of the ketone **18b**, mp 175–178°, which was obtained as 663 mg of yellow needles, mp 184.5–185°, after recrystallization from $CHCl_3$–EtOH. An additional recrystallization from acetone gave yellow needles, mp 182–183°, which resolidified and remelted with decomposition at 192–193°: ir ($CHCl_3$) 1680 (conjugated C=O), 1615 (sh), and 1605 cm^{-1} (C=C); uv (CH_2Cl_2) 405 mμ (ε 33,200). When several equivalents of CF_3CO_2H were added to form the salt **19b**, the maximum was at 563 mμ (ε 70,500); nmr ($CDCl_3$) δ 7.92 (s, 1 H, vinyl CH), 6.8–7.4 (m, 6 H, aryl CH), 4.44 (t, 2 H, J = 7 Hz, ethoxyl CH_2), 3.80 (s, 6 H, OCH_3), 3.65 (s, 2 H, benzylic CH_2), 3.50 (s, 2 H, benzylic CH_2), and 1.48 (t, 3 H, J = 7 Hz, ethoxyl CH_3).

Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.16; H, 6.22.

The same ketone **18b** was also obtained in 87.5% yield by treatment of the salt **17b** with aqueous EtOH or by direct partitioning of the original reaction mixture between aqueous EtOH and CH_2Cl_2. When the ketone **18b** was dissolved in CF_3CO_2H and the nmr spectrum was determined promptly, the spectrum of the cation **19b** was obtained: δ 8.63 (s, 1 H, vinyl CH), 7.2–7.7 (m, 6 H, aryl CH), 4.97 (q, 2 H, J = 7 Hz, ethoxyl CH_2), 3.95 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.70 (br s, 4 H, aliphatic CH), and 1.70 (t, 3 H, J = 7 Hz, ethoxyl CH_3). When this solution was allowed to stand, the nmr spectrum changed. When the ketone **18b** was dissolved in CF_3CO_2H containing 10% $(CF_3CO)_2O$, a different nmr spectrum was obtained which we assign to the trifluoroacetyl salt **20**: nmr [100 MHz, 10% $(CF_3CO)_2O$ in CF_3CO_2H] δ 8.44 (s, 1 H, vinyl CH), 7.82 (partially resolved m, 3 H, aryl CH), 7.70 (d, 1 H, J = 8.5 Hz, aryl CH), 7.37 (d of d, 1 H, J = 8.5 and 2.0 Hz, aryl CH), 7.12 (d, 1 H, J = 2.0 Hz, aryl CH), 5.47 (q, 2 H, J = 7 Hz, ethoxyl CH_2), 4.20 (s, 2 H, benzylic CH_2), 4.09 (s, 2 H, benzylic CH_2), 4.04 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), and 1.87 (t, 3 H, J = 7 Hz, ethoxyl CH_3).

Hydrogenation of the Ketone 18a.—A solution of 1.812 g (6.0 mmol) of the ketone **18a** in 55 ml of HOAc was hydrogenated 26° (1 atm) over 50 mg of a 5% Pd-C catalyst. The reaction was stopped after 8 hr, at which time 29.1 mmol of the H_2 had been absorbed. The mixture was filtered and concentrated to leave a partially crystalline residue which was chromatographed (silica gel). The earlier fractions (PhH eluent) contained 724 mg (48%) of the hydrocarbon **21** which was obtained as colorless needles: mp 71–71.5° (lit.[15] mp 69.9–70.5°), after recrystallization from MeOH; ir (CCl_4) no OH or C=O in 3- or 6-μ region; nmr (CCl_4) δ 7.0 (br s, 8 H, aryl CH), and 1.4–3.2 (m, 12 H, aliphatic CH). The second compound (PhH eluent) was obtained as 189 mg of a partially characterized liquid which may be the ketal **23**: ir (CCl_4) 1075 and 1120 cm^{-1} (ether CO); nmr (CCl_4) δ 7.10 (m, 8 H, aryl CH), 4.45 and 5.0 (2 d, 1 H, J = 4.8 and 7.2 Hz, CHO in *cis* and *trans* isomers), 1.50–3.70 (m, 10 H, ethoxyl CH_2 and aliphatic CH), and 1.10 (t, 3 H, J = 7 Hz, ethoxyl CH_3).



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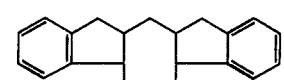

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The third component (5% EtOAc in PhH eluent) was 571 mg (36%) of the alcohol **22**, mp 117–118.5°, which melted at 119.5–120.5° (lit.[15] mp 119–120°) after recrystallization from acetone: ir ($CHCl_3$) 3580 and 3420 (br) cm^{-1} (OH); nmr ($CDCl_3$) δ 7.2 (m, 8 H, aryl CH), 4.75 (d, 1 H, J = 6 Hz, CHO probably with *cis* H atoms at C-1 and C-2 of the indane ring), and 1.6–3.3 (m, 11 H, OH and aliphatic CH).

Continued elution (5% EtOAc in PhH) separated 84 mg (4.5%) of an additional minor, partially characterized product which crystallized from hexane as 55 mg of colorless needles: mp 101.5–102°; ir (CCl_4) 3620 (sh) and 3590 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.2 (m, 8 H, aryl CH), 4.83 (d, 1 H, J = 6.0 Hz, CHO), 4.63 (d, 1 H, J = 4.8 Hz, CHO), 1.7–3.70 (m, 10 H, ethoxyl CH_2 and aliphatic CH), 2.10 (s, 1 H, exchanged with D_2O, OH), and 1.15 (t, 3 H, J = 7 Hz, ethoxyl CH_3). This material may be the hydroxy ether **24**.

Registry No.—**2**, 13623-25-1; **5**, 22955-82-4; **7**, 22955-73-3; **8**, 22955-74-4; **9b**, 22955-75-5; **13a**, 22955-77-7; **13b**, 22955-78-8; **14**, 22955-79-9; **15**, 22955-80-2; **17a**, 23016-03-7; **17b**, 23016-04-8; **18a**, 22955-81-3; **18b**, 22950-35-2; **19a**, 22966-46-7; **19b**, 23016-05-9; **20**, 22950-36-3; **21**, 22950-37-4; **22**, 22950-38-5; **23**, 22950-39-6; **24**, 22950-40-9; dimethyl 3-(4-methoxybenzyl)-2-ketosuccinate, 22955-76-6.

(15) M. G. J. Beets and H. van Essen, *Rec. Trav. Chem. Pays-Bas*, **61**, 343 (1952).