as in method B, with the exception that where ethylene glycol was used, the reaction temperature was 100°.

Registry No.—I, 15038-67-2; III, 14909-73-0; IV, 14909-74-1; acetate of IV, 14909-75-2; V, 14909-76-3; VI, 14909-77-4.

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A Study of the *p*-Methoxybenzylidene Derivatives of Succinic and Malonic Acids[1a]

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An interest in the methoxyindenone **1** as a possible synthetic intermediate for certain gibberellins lead us to study several transformations of the Stobbe condensation product **2** (Scheme I). Based on previous studies[2] of acid-catalyzed intramolecular acylations, we anticipated that cyclization of the *trans* acid **2** or anhydride **3** would yield the naphthol **4**, whereas cyclization of the *cis* acid **5** or one of its derivatives **6** or **7** might yield the desired indenone **1**. The indicated photochemical isomerizations ($2 \rightleftharpoons 5$ and $8 \rightleftharpoons 7$) provided the previously unknown *cis* acid **5** and its derivatives. A variety of attempts to convert the *cis* acid **5**, *cis* anhydride **6**, or derivatives of the *cis*-monomethyl ester **7** to the indenone **1** resulted in formation of the naphthol **4**, the *trans* anhydride **3**, or intractable materials. It appears that the acid-catalyzed interconversion of the *cis* and *trans* anhydrides is more rapid than cyclization, presumably because of the charge delocalization possible in the acyl cation **16** which gives this intermediate a sufficiently long lifetime to permit *cis–trans* isomerization.[2c]

Because of the reported[3] difficulties in acid-catalyzed cyclizations of 3-(4-methoxyphenyl)propionic acid derivatives (**13**) and related materials, we examined briefly the cyclization of the pure acid chloride **13c** under various conditions (Scheme II). Cyclization in the presence of aluminum chloride and methylene chloride gave a moderate yield (38%) of the indanone **15** (no attempt was made to optimize this yield). In earlier work,[3a,b] the addition of a benzene solution of the acid chloride **13c** to aluminum chloride had been found to give the indanone **15** in 93–100% yield. Repeated attempts to duplicate this result gave mixtures of the indanone **15** (*ca.* 20% yield) and the previously unreported phenyl ketone **14** (*ca.* 40% yield). It is possible that this differing behavior of benzene solutions of the acid chloride **13c** is attributable to a significant difference in the quality and purity of the commercial aluminum chloride available at the times when the two sets of experiments were performed.

Experimental Section[4]

Preparation of the *trans* Acid 2 and Its Derivatives.—Following previously described procedures,[5] the diacid **2** was obtained as white needles from water: mp 193–201° dec (decomposition temperature dependent on rate of heating) (lit. mp 202–203°,[5b] 188–191°,[6a] 194–195°[6b]); ultraviolet maximum, 290 mμ (ϵ 20,500); infrared (KBr), 1695 (carboxyl $C{=}O$), 1670 (conjugated carboxyl $C{=}O$), and 1602 cm^{-1} (conjugated $C{=}C$); nmr ($(CD_3)_2NCDO$), δ 7.89 (1 H singlet, vinyl C–H), 7.54 (2 H doublet with $J = 9$ cps, aryl CH), 7.11 (2 H doublet with $J = 9$ cps, aryl CH), 3.89 (3 H singlet, O–CH_3), and 3.59 (2 H singlet, CH_2–CO). Reaction of the *trans* acid **2** with acetic anhydride afforded the anhydride **3** which crystallized from a benzene–cyclohexane mixture as colorless plates: mp 161–162° (lit.[5a] mp 166–167°); infrared ($CHCl_3$), 1840 and 1770 cm^{-1} (anhydride $C{=}O$) and 1645 cm^{-1} (conjugated $C{=}C$); ultraviolet maximum (CH_3CN), 233 mμ (ϵ 9900) and 321 (29,800); nmr ($(CD_3)_2NCDO$), δ *ca.* 7.7 (1 H superimposed on an adjacent peak, vinyl CH), 7.77 (2 H doublet with $J = 9$ cps, aryl CH), 7.16 (2 H doublet with $J = 9$ cps, aryl CH), *ca.* 4.1 (2 H, partially resolved AB pattern with $J \sim 20$ cps, CH_2–CO), and 3.94 (3 H singlet, O–CH_3).

Reaction of the anhydride **3** with methanol yielded, after crystallization from a benzene–cyclohexane mixture, the monomethyl ester **8** as white needles: mp 136–137° (lit.[5a] mp 139–140°); infrared ($CHCl_3$), 1735 (ester $C{=}O$), 1680 (conjugated carboxyl $C{=}O$), and 1630 cm^{-1} (conjugated $C{=}C$); ultraviolet maximum, 289 mμ (ϵ 19,700); nmr ($CDCl_3$), δ 8.04 (1 H singlet, vinyl CH), 7.42 (2 H doublet with $J = 9$ cps, aryl CH), 6.99 (2 H doublet with $J = 9$ cps, aryl CH), 3.87 (3 H singlet, O–CH_3), 3.79 (3 H singlet, O–CH_3), and 3.63 (2 H singlet, CH_2–CO); pK_{MCS}^* 6.82.[7]

In the preparation of the acid **2**, a minor higher melting by-product, the diarylidene acid **9**, was isolated as a yellow solid: mp 254–257° dec (decomposition point dependent on rate of heating) (lit.[5c] mp 260–261°); infrared (KBr), 1675 cm^{-1} (conjugated carboxyl $C{=}O$). Reaction of this diacid **9** with acetic anhydride followed by recrystallization from a benzene–hexane mixture gave the anhydride **10** (stereochemistry unknown) as yellow plates: mp 174–176° (lit.[5c] mp 179–180°); infrared ($CHCl_3$), 1760 and 1820 cm^{-1} (anhydride $C{=}O$); ultraviolet maxima (CH_3CN), 227 mμ (ϵ 14,100), 255 (10,100), 319 (27,700), and 407 (14,000); nmr ($CDCl_3$), δ 7.89 (2 H singlet, vinyl C–H), 6.76 (4 H doublet, $J = 9$ cps, aryl CH), 6.46 (4 H doublet, $J = 9$ cps, aryl CH), and 3.78 (6 H singlet, O–CH_3).

Preparation of the *cis* Acid 5 and Its Derivatives.—A solution of the disodium salt derived from 37 g (0.16 mole) of the *trans* acid **2** in 300 ml of water was irradiated under a nitrogen atmosphere with a Hanovia mercury lamp (450 w) for 24 hr. The solution was acidified and the crude acid was collected and fractionally crystallized from water to separate 10 g (27%) of the less soluble starting *trans* acid **2** and 18 g (49%) of the more soluble *cis* acid **5** as a white solid: mp 165–168° dec (decomposition point dependent on rate of heating); infrared (KBr), 1705

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[2] (a) W. S. Johnson, *Org. Reactions*, **2**, 114 (1944); (b) W. S. Johnson and G. H. Daub, *ibid.*, **6**, 1 (1951); (c) W. S. Johnson and R. P. Graber, *J. Am. Chem. Soc.*, **72**, 925 (1950).

[3] (a) W. S. Johnson and W. E. Shelberg, *ibid.*, **67**, 1853 (1945); (b) W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949); (c) J. Sam and J. N. Plampin, *ibid.* **82**, 5205 (1960).

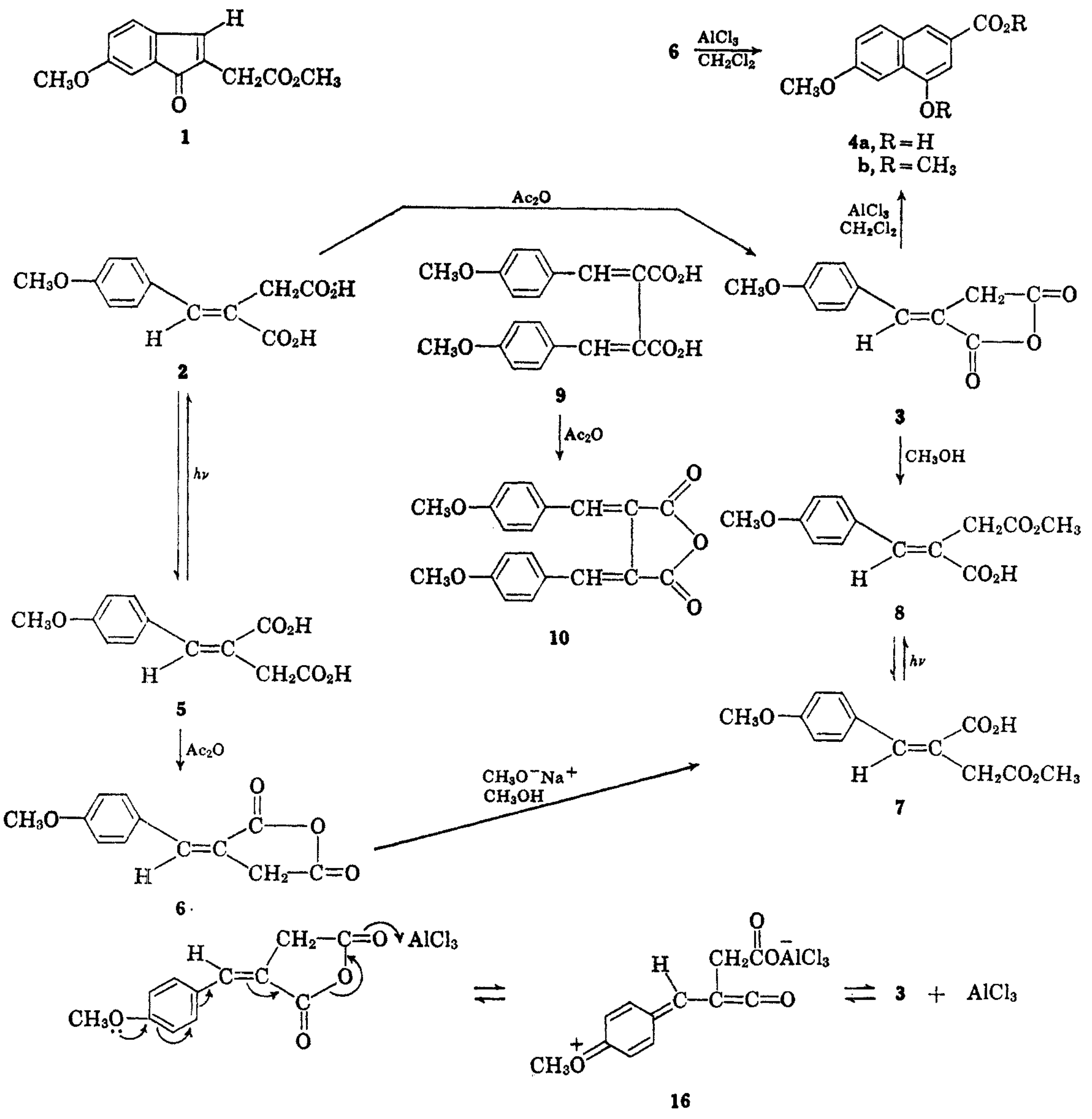
[4] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. Unless otherwise noted, all 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 or δ values (parts per million) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC Model 21-130 mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

[5] (a) A. M. El-Abbady and L. S. El-Assal, *J. Chem. Soc.*, 1024 (1959); (b) F. G. Badder, L. S. El-Assal, N. A. Doss, and A. H. Shehab, *ibid.*, 1016 (1959); (c) F. G. Baddar, L. S. El-Assal, and M. Gindy, *ibid.*, 1270 (1948).

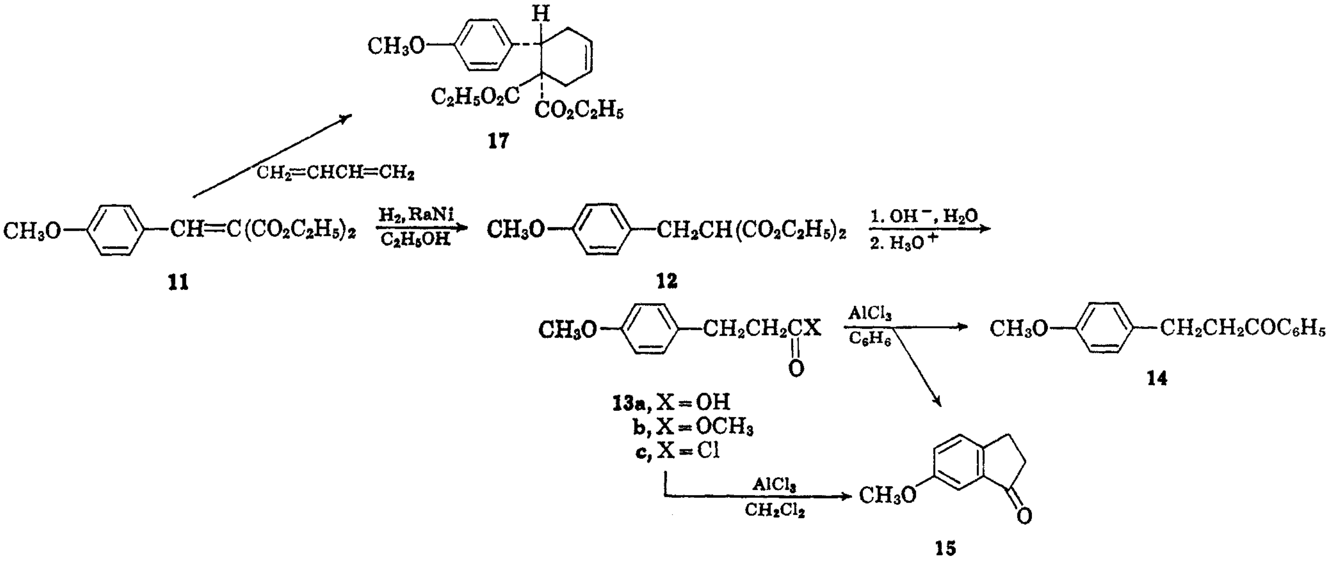
[6] (a) K. N. Campbell, J. A. Cella, and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 4681 (1953); (b) A. L. S. Buckle, A. McGookin, and A. Robertson, *J. Chem. Soc.*, 3981 (1954).

[7] The values pK_{MCS}^*, the apparent pK_a value in a mixture of 80% Methyl Cellosolve and 20% water, were determined by Dr. W. Simon. For discussion and leading references, see W. Simon, *Angew. Chem. Intern. Ed. Engl.*, **3**, 661 (1964)

SCHEME I



SCHEME II



and 1670 cm^{-1} (unconjugated and conjugated carboxyl C=O); ultraviolet maximum, 283 mμ (ε 15,700).

Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.13. Found: C, 61.03; H, 5.16.

A solution of 5.11 g (21.7 mmoles) of the *cis* diacid **5** in 15 ml of acetic anhydride was heated to 100° for 1 hr and then cooled to separate 3.78 g (80%) of the anhydride **6**, mp 159–163°. Recrystallization from a benzene–cyclohexane mixture gave the pure anhydride **6** as white plates: mp 163–166°;[8] infrared ($CHCl_3$), 1840 and 1770 (anhydride C=O), and 1630 cm^{-1} (conjugated C=C); ultraviolet maxima (CH_3CN), 330 mμ (ε 20,400), 236 (8950), and 223 (7960); nmr (($(CD_3)_2NCDO$), δ 8.07 (2 H doublet, J = 9 cps, aryl CH), 7.25 (1 H multiplet, vinyl CH), 7.06 (2 H doublet, J = 9 cps, aryl CH), 3.95 (2 H, center of a partially resolved AB pattern, CH_2–CO), and 3.89 (3 H singlet, O–CH_3).

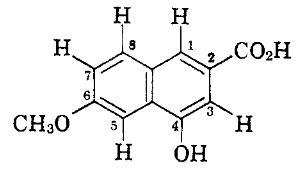
Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.07; H, 4.70.

A solution of 436 mg (2.0 mmoles) of the anhydride **6** and 2.0 mmoles of sodium methoxide in 45 ml of methanol was stirred at 25° for 30 min and then concentrated, diluted with water, and acidified. The crude monoacid was collected and recrystallized from a benzene–cyclohexane mixture to separate 153 mg (31%) of the pure *cis* monoester **7** as white needles, mp 97.5–100°, identified with the subsequently described sample by a mixture melting point determination. Alternatively, a solution of 20 g (0.080 mole) of the *trans* monoester **8** in 150 ml of benzene and 350 ml of ethyl acetate was irradiated with a Hanovia mercury lamp (450 w) for 45 min and then concentrated. A series of fractional crystallizations from benzene separated 9.0 g (45%) of the starting *trans* monoester **8** and 569 mg (2.8%) of the pure *cis* monoester **7**: mp 98–100°; infrared ($CHCl_3$), 1735 (ester C=O) and 1690 cm^{-1} (carboxyl C=O); ultraviolet maximum, 284 mμ (ε 12,400); nmr ($CDCl_3$), δ 7.30 (2 H doublet, J = 9 cps, aryl CH), *ca.* 6.8 (1 H singlet superimposed on one peak of the following doublet, vinyl CH), 6.75 (2 H doublet, J = 9 cps, aryl CH), 3.76 (3 H singlet, O–CH_3), 3.67 (3 H singlet, O–CH_3), and 3.40 (2 H singlet, CH_2–CO); pK_{MCS}*, 6.37.[7]

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.26; H, 5.75.

The relative positions of the nmr signals for the vinyl protons and the $-CH_2CO_2R$ protons of the monoesters and the anhydrides are consistent with the assigned stereochemistry. The vinyl protons of the *trans* isomers **3** and **8** (shielded by a *cis* carbonyl function) are at lower field than the signals for the *cis* isomers **6** and **7**. Also, the methylene signals for the *trans* isomers **3** and **8** (shielded by the *cis*-*p*-methoxyphenyl groups) are at lower field than the signals for the *cis* isomers **6** and **7**.

Reactions of the Anhydrides with Aluminum Chloride. A. The *trans* Isomer 3.—Aluminum chloride (1.34 g or 10 mmoles) was added to a solution of 1.0 g (4.2 mmoles) of the anhydride **3** in 50 ml of methylene chloride and the resulting yellow solution was stirred at room temperature for 45 min during which time a green precipitate separated. The reaction mixture was hydrolyzed with ice and aqueous acid. The crude product separated as a white solid (902 mg or 98%) which was recrystallized from aqueous ethanol to separate 260 mg (28%) of the pure hydroxy acid **4a** as light tan needles: mp 243–246° dec;[9] infrared (KBr and Nujol mull), 3450 (br, OH), *ca*, 3000 (br, carboxyl OH), and 1655 cm^{-1} (carboxyl C=O); ultraviolet maxima, 256 mμ (ε 40,900), 312 (7300), 327 (5900), and 343 (4700); nmr (($(CD_3)_2$-NCDO), δ 4.01 (3 H singlet, O–CH_3, 7.28 (1 H quartet, J = 9 and 2.5 cps, C_7–H), 8.00 (1 H doublet, J = 9 cps, C_8–H), 8.17 (1 H, br singlet, C_1–H), and 7.63 (2 H multiplet, superimposed signals for C_5–H and C_3–H).



Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.19; H, 4.64.

Because of the disagreement in melting behavior of the hydroxy acid **4a**,[9] a solution of 218 mg (1.0 mmole) of this hydroxy acid in 15 ml of aqueous 10% NaOH was treated with 2.0 g of dimethyl sulfate and the resulting mixture was stirred for 13 hr. After the resulting mixture had been extracted with ethyl acetate, it was acidified and again extracted with ethyl acetate. The acidic product recovered from the ethyl acetate was recrystallized from aqueous ethanol to separate 121 mg of 4,6-dimethoxy-2-naphthoic acid as white needles, mp 263–266° (lit.[5a] mp 262–263°). Reaction of this acid with excess ethereal diazomethane yielded the methyl ester **4b** which separated from methanol as white needles: mp 90–92° (lit.[5a] mp 104–105°); infrared (CCl_4), 1725 cm^{-1} (ester C=O); ultraviolet maxima, 215 mμ (ε 29,900), 256 (41,300), 311 (10,100), 324 (8000), and 340 (5600); nmr (CCl_4), δ 7.0–8.3 (5 H multiplet, aryl CH), 4.04 (3 H singlet, OCH_3), 3.93 (3 H singlet, OCH_3), and 3.89 (3 H singlet, OCH_3).

B. The *cis* Isomer 6.—The same cyclization procedure was applied to 1.0 g (4.2 mmoles) of the *cis* anhydride **6** to yield 764 mg (83%) of crude product which was recrystallized from aqueous ethanol to separate 452 mg (49%) of the hydroxy acid **4a**, mp 246–250 dec. This material was identified with the previous sample by a mixture melting point determination and comparison of infrared spectra.

Diethyl *p*-Methoxybenzylidenemalonate (11) and Its Transformation Products.—Use of a standard procedure[10] yielded 78% of the arylidenemalonate **11**, bp 130–147° (0.13 mm), which crystallized as a white solid: mp 35–37° (lit.[11] mp 38–40°, bp 200–217° (14 mm)); infrared ($CHCl_3$), 1715 (conjugated ester C=O) and 1620 cm^{-1} (conjugated C=C); ultraviolet maxima, 229 mμ (ε 15,600) and 313 (25,500); nmr ($CDCl_3$), δ 7.60 (1 H singlet, vinyl CH), 7.37 (2 H doublet, J = 9 cps, aryl CH), 6.83 (2 H doublet, J = 9 cps, aryl CH), 4.33 and 4.26 (4 H, two overlapping quadruplets, J = 7 cps for each, O–CH_2), 3.78 (3 H singlet, O–CH_3), and 1.30 (6 H triplet, J = 7 cps, CH_3–C).

An ethanol solution of the arylidenemalonate **11** was hydrogenated at 25° and 1-atm pressure over an active Raney nickel catalyst[12] to yield 91% of the malonate **12** as a colorless liquid: bp 138–142° (0.2 mm); $n^{27}D$ 1.4928 (lit.[13] bp 192–193° (12 mm)); infrared (CCl_4), 1755 and 1735 cm^{-1} (ester C=O); ultraviolet maxima, 226 mμ (ε 11,500), 277 (1650), and 283 (1380); nmr (CCl_4), δ 7.06 (2 H doublet, J = 9 cps, aryl CH), 6.72 (2 H doublet, J = 9 cps, aryl CH), 4.11 (4 H quadruplet, J = 7 cps, O–CH_2–), 3.72 (3 H singlet, O–CH_3), 2.9–3.6 (3 H multiplet, aliphatic CH), and 1.18 (6 H triplet, J = 7 cps, CH_3–C). Saponification and subsequent decarboxylation of this malonic ester **12** gave, after recrystallization from a benzene–cyclohexane mixture, acid **13a** as white plates, mp 103.5–104° (lit.[3a] mp 103.5–104°). A portion of acid **13a** was esterified with ethereal diazomethane to yield the methyl ester **13b** as white plates from petroleum ether (bp 30–60°): mp 35–36° (lit.[14] mp 38°): infrared (CCl_4), 1740 cm^{-1} (ester C=O); ultraviolet maxima, 224 mμ (ε 10,400), 277 (1840), and 283 (1530); nmr (CCl_4), δ 6.92 (2 H doublet, J = 9 cps, aryl CH), 6.60 (2 H doublet, J = 9 cps, aryl CH), 3.61 (3 H singlet, OCH_3), 3.50 (3 H singlet, OCH_3), and 2.2–2.9 (4 H multiplet, aliphatic CH). Reaction of acid **13a** with oxalyl chloride yielded 88% of the acid chloride **13c** as a colorless liquid: bp 95–97° (0.2 mm) (lit.[15] bp 161–165° (15 mm)); infrared (CCl_4), 1805 cm^{-1} (acid chloride C=O); nmr (CCl_4), δ 7.07 (2 H doublet, J = 9 cps, aryl CH), 6.78 (2 H doublet, J = 9 cps, aryl CH), 3.76 (3 H singlet, O–CH_3), and 2.7–3.2 (4 H multiplet, aliphatic CH).

Reaction of the Acid Chloride 13c with Aluminum Chloride. A. In Benzene Solution.—To a cold (5°) suspension of 3.10 g (23 mmoles) of aluminum chloride in 15 ml of benzene was added, dropwise and with stirring, a solution of 2.75 g (13.9

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[8] A mixture of the two anhydrides **3** and **6** melted at 120–130°.

[9] A compound, mp 200–201° dec, described as the crude hydrate of the acid **4a** was reported[5a] to be formed by reaction of the monomethyl ester of acid **2** with boiling acetic anhydride containing sodium acetate followed by saponification. This material gave a different solid, mp 252–254°, after it had heated in acetic acid.[5a] Since we had no indication that our hydroxy acid **4a** formed a stable hydrate and we found acetic anhydride converted the diacid **2** to an anhydride **3**, we are led to suggest that the previous material, mp 200–201° dec, was in fact not the hydroxy acid **4a** but rather, at least in part, the diacid **2**.

[10] C. F. H. Allen and F. W. Spangler, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 377.

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

[12] X. A. Dominguez, I. C. Lopez, and P. Franco, *J. Org. Chem.*, **26**, 1625 (1961).

[13] M. M. Jacques and A. Horeau, *Bull. Soc. Chim. France*, 512 (1950).

[14] G. Eigel, *Ber.*, **20**, 2533 (1887).

[15] G. Barger and G. S. Walpole, *J. Chem. Soc.*, **95**, 1724 (1909).

mmoles) of the acid chloride in 20 ml of benzene. After the addition was complete, the reaction mixture was stirred for 4 hr at 25° and then poured into cold, aqueous HCl. The organic layer was combined with the ethyl acetate extract of the aqueous phase and the combined organic solutions were washed with aqueous $NaHCO_3$, dried, and concentrated. Chromatography of the residual oil (2.36 g) on silicic acid separated 1.35 g (40%) of the phenyl ketone **14** (mp 62–63°) in the early fractions eluted with hexane–ether mixtures and 469 mg (21%) of the indanone **15** in the later fractions eluted with the same solvent mixture. The pure **phenyl ketone 14** crystallized from cyclohexane as white needles: mp 62–63°; infrared (CCl_4), 1680 cm^{-1} (conjugated C═O); ultraviolet maxima, 228 mμ (ϵ 13,300), 242 (13,200), 278 (2810), and 284 (shoulder, ϵ 2380); nmr ($CDCl_3$), δ 7.3–8.0 (5 H multiplet, phenyl C–H), 7.10 (2 H doublet, J = 9 cps, aryl CH), 6.77 (2 H doublet, J = 9 cps, aryl CH), 3.73 (3 H singlet, O–CH_3), and 2.8–3.4 (4 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.79; H, 6.68.

The pure **indanone 15** crystallized from cyclohexane solution as white needles: mp 108–109° (lit.[3] mp 108–108.5°); infrared (CCl_4), 1715 cm^{-1} (conjugated C═O in a five-membered ring); ultraviolet maxima, 217 mμ (ϵ 23,500), 248 (9950), and 319 (4480); nmr ($CDCl_3$), δ 7.2–7.6 (3 H multiplet, aryl CH), 3.92 (3 H singlet, O–CH_3), and 2.5–3.4 (4 H multiplet, aliphatic CH).

In an effort to learn why our reaction in benzene solution yielded both the indanone **15** and the phenyl ketone **14** whereas similar reaction conditions had been reported earlier[3] to form the indanone **15** in high yield, we attempted to duplicate exactly the early reaction conditions.[3a,b] Reaction of 1.00 g (5.5 mmoles) of the acid **13a** with 1.27 g (6.1 mmoles) of phosphorus pentachloride in 10 ml of benzene was effected as previously described.[3a,b] From a solution of the crude product in 15 ml of benzene, a 1.5-ml aliquot was separated and distilled in a short-path still. The distillate (34 mg) was identified as the previously described acid chloride **13c** by comparison of infrared spectra. The crude residue, 61 mg of a high-boiling liquid, had infrared absorption (CCl_4) at 1820 and 1760 cm^{-1}, suggesting that the residue was the crude anhydride derived from acid **13a**. The remaining benzene solution (13.5 ml equivalent to 5.0 mmoles of acid chloride **13c**) was added to 0.96 g (7.2 mmoles) of aluminum chloride as previously described. A solution of this crude product in ethyl acetate was washed successively with aqueous HCl, aqueous NaOH, and water and then dried and concentrated to leave 385 mg of crude neutral product, mp 70–78°. Chromatography on silicic acid separated 105 mg (9%) of the pure phenyl ketone **14**, mp 60–62°, and 134 mg (17%) of the indanone **15**, mp 105–108°. After recrystallization the products melted at 61–62 and 107–108°, respectively. Each material was identified with the previously described sample by comparison of infrared spectra.

B. In Methylene Chloride Solution.—To a cold (0°) suspension of 3.10 g (23 mmoles) of aluminum chloride in 20 ml of methylene chloride was added, dropwise and with stirring, a solution of 3.12 g (15.8 mmoles) of the acid chloride **13c** in 20 ml of methylene chloride. The resulting mixture was stirred for 4 hr at room temperature and then subjected to the previously described isolation procedure. The crude neutral product was chromatographed on silicic acid to separate the crude indanone **15** (975 mg or 38%) in fractions eluted with an ether–hexane mixture. Recrystallization from cyclohexane separated 465 mg (18%) of the pure **indanone 15**, mp 107–108°, identified with the previously described sample by a mixture melting point determination and comparison of infrared spectra.

Preparation of the Diels–Alder Adduct 17.—A solution of 20.0 g (0.072 mole) of the arylidenemalonate **11**, 15 ml of 1,3-butadiene, and 1.0 g of 2,5-di-*t*-butyl-1,4-hydroquinone (as inhibitor) in 80 ml of benzene was heated in an autoclave to 200° for 50 hr and then cooled, concentrated, and distilled. The distillate, 14.5 g collected at 145–165° (0.25 mm), contained[16] approximately equal amounts of the starting conjugated ester **11** (eluted first) and the adduct **17** (eluted second). A solution of this material in 50 ml of ether was stirred with excess aqueous 10% NaOH to effect selective saponification of the starting ester **11**. The ether solution (containing[16] *ca.* 8% of **11** and *ca.* 92% of **17**) was dried, concentrated, and distilled in a short-path still, 155–165° (0.3 mm), to separate 2.12 g (8.9%) of the adduct **17** as a colorless liquid which crystallized on standing, mp 53–56°. Recrystallization from a benzene–petroleum ether (bp 30–60°) mixture afforded the adduct **17** as white prisms: mp 53–56°; infrared ($CHCl_3$), 1735 cm^{-1} (ester C═O); ultraviolet maxima, 226 mμ (ϵ 12,700), 276 (1650), 283 (1490), and 312 (224); nmr ($CDCl_3$), δ 7.21 (2 H doublet, J = 9 cps, aryl CH), 6.81 (2 H doublet, J = 9 cps, aryl CH), 5.85 (2 H broad singlet, vinyl, CH), 4.17 and 4.07 (4 H overlapping quadruplets, J = 7 cps, CH_2–O), 3.78 (3 H singlet, O–CH_3), 3.6–3.8 (1 H multiplet, benzylic CH), 2.1–3.0 (4 H multiplet, aliphatic CH), and 1.17 (6 H triplet, J = 7 cps, CH_3–C).

Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.53; H, 7.03.

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[16] A gas chromatography column packed with silicone gum, no. SE-30, suspended on Chromosorb P was employed for this analysis.

Thermolysis Reactions of Biphenylene

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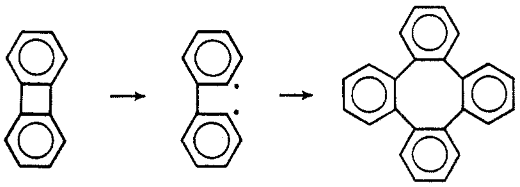
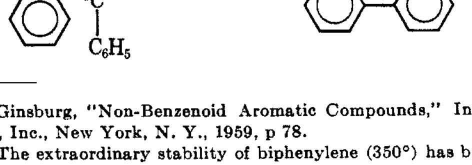
The question of biphenylene "inner ring" chemistry was discussed in 1959 by Baker and McOmie,[1] but attempts at experimental verification were unsuccessful. Thus it had been concluded that even though the biphenylene "inner ring" may be highly strained, it is very stable and, in general, unreactive. This present work shows that biphenylene "inner ring" chemistry does, in fact, exist.[2]

Previous work in this laboratory[3] has shown that under thermolytic conditions biphenylene undergoes bond fission which can lead to dimerization and the formation of tetraphenylene. The present study examines the thermolysis of biphenylene in the presence of other acceptors.



When biphenylene was heated to 350–375° (under N_2) in the presence of a fivefold excess of diphenylacetylene, 9,10-diphenylphenanthrene was formed in about 50% yield (gas chromatography) based on biphenylene.



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[1] D. Ginsburg, "Non-Benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, p 78.

[2] (a) The extraordinary stability of biphenylene (350°) has been noted previously: W. Baker and J. McOmie, Chemical Society Symposia, Bristol, 1958, Special Publication No. 12, The Chemical Society, London, pp 49–67. (b) Biphenylene has been treated with hexacarbonylchromium to provide fluorenone in low yield. This reaction, however, may not be mechanistically comparable to the present study; see E. Atkinson, P. Levins, and T. Dickelman, *Chem. Ind.* (London), 930 (1964).

[3] D. Lindow and L. Friedman, *J. Am. Chem. Soc.*, **89**, 1271 (1967); L. Friedman and D. Lindow, *ibid.*, in press.