Lactones. IX. Reactions of Highly Conjugated Butenolides under Friedel–Crafts Conditions. Synthesis of Polynuclear and Aryl-substituted Butadiene Carboxylic Acids[1-3]

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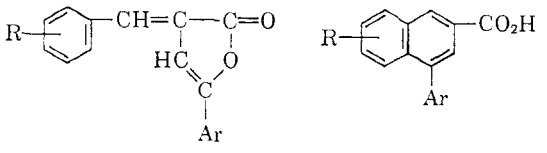
In the presence of anhydrous aluminum chloride and excess benzene, α-arylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolides are converted to polycyclic hydrocarbon carboxylic acids or 1,1-diphenyl-4-aryl-1,3-butadiene-3-carboxylic acids by *intramolecular* and *intermolecular* alkylation, respectively. The type of product is strongly dependent on the nature of substituents on the arylidene ring. The effects of solvent, catalyst, and temperature variations have been examined. The acids were decarboxylated to the parent hydrocarbons.

The conversion of γ-lactones to naphthalene derivatives has been described by a number of investigators.[4-9] We have recently reported[8] the facile isomerization of α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (Ia) to 4-phenyl-2-naphthoic acid (IIa) by anhydrous aluminum chloride in benzene solvent. It was proposed that intramolecular alkylation proceeds *via* electrophilic attack at the *ortho* position of the arylidene ring by a resonance-stabilized carbonium ion, generated by alkyl-oxygen bond cleavage, with the assistance of aluminum chloride. The driving force for the cyclization is the stabilization afforded by the newly formed aromatic system.

We report here a more detailed study of the scope and limitations of the reaction of highly conjugated butenolides under Friedel–Crafts conditions.



Ia. R = H, Ar = C_6H_5 IIa. R = H, Ar = C_6H_5

Results and Discussion

The butenolides (I) were prepared in 32–71% yields by the reaction of aromatic or heterocyclic aldehydes (acetophenone failed to react) with 3-benzoylpropionic acid in the presence of acetic anhydride and anhydrous sodium acetate. Electron-attracting substituents (*e.g.*,—NO_2) enhanced the yield, in agreement with observations on the mechanistically similar Perkin synthesis of cinnamic acids.[10] It has recently been shown that butenolides[11] and the structurally similar azlactones[12] may be isolated in improved yields by using the sulfur trioxide–dimethylformamide complex in place of the anhydride–acetate combination.

The multiple functionality of the butenolides offers a potential treasure of chemical reactivity, so that these compounds represent extremely versatile intermediates in organic synthesis. The reactive lactone ring is readily opened (acyl–oxygen cleavage) by nucleophiles[13,14] to give α-phenacylcinnamic acid derivatives and related cyclic structures. Grignard reagents add 1,4 to the α,β-unsaturated carbonyl system,[14] with the lactone ring remaining intact.

The highly conjugated carbon chain provides a third avenue for attack and this is the reactive site in the Friedel–Crafts reaction.

The behavior of the butenolides in excess benzene at 25°, in the presence of aluminum chloride, followed two distinct courses, both involving alkylation, but dependent on the nature of the arylidene ring and of the R substituent on that ring. The results are summarized in the chart.

With the benzylidene- and *o*- and *p*-chlorobenzylidenebutenolides, benzene served only as a solvent, and intramolecular alkylation occurred to give IIa and the corresponding (8-chloro- and 6-chloro-)-4-phenylnaphthalene-2-carboxylic acids in 31–82% yields. Similarly, the 1-naphthylidene analog was converted to 4-phenylphenanthrene-2-carboxylic acid in 21% yield.

However, when the substituent was an *ortho* or *para* methoxyl group or when 2-furylidene replaced benzylidene, *intermolecular alkylation* of benzene led to 1,1-diphenyl-4-aryl-1,3-butadiene-3-carboxylic acids (III) in 52–81% yields. This type of behavior has been observed previously[15]

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(2) Abstracted, in part, from the M.S. thesis of Hans A. Leipold, June, 1962.

(3) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961. Paper VIII, R. Filler and Y. S. Rao, *J. Org. Chem.*, **27**, 3730 (1962).

(4) R. D. Haworth and G. J. Sheldrick, *J. Chem. Soc.*, 636 (1935).

(5) W. N. Howell and A. Robertson, *ibid.*, 587 (1936).

(6) L. S. El-Assal and A. H. Shehab, *ibid.*, 1020 (1959).

(7) L. S. El-Assal and A. H. Shehab, *ibid.*, 1658 (1961).

(8) R. Filler, L. H. Mark, and E. J. Piasek, *J. Org. Chem.*, **24**, 1780 (1959).

(9) H. Beyer and U. Hess, *Ber.*, **94**, 1717 (1961)

(10) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1954, p. 774.

(11) E. Baltazzi, personal communication.

(12) E. Baltazzi and E. A. Davis, *Chem. Ind.* (London), 929 (1962).

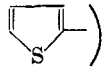
(13) R. Filler and L. M. Hebron, *J. Am. Chem. Soc.*, **81**, 391 (1959).

(14) R. Filler, E. J. Piasek, and L. H. Mark, *J. Org. Chem.*, **26**, 2659 (1961).

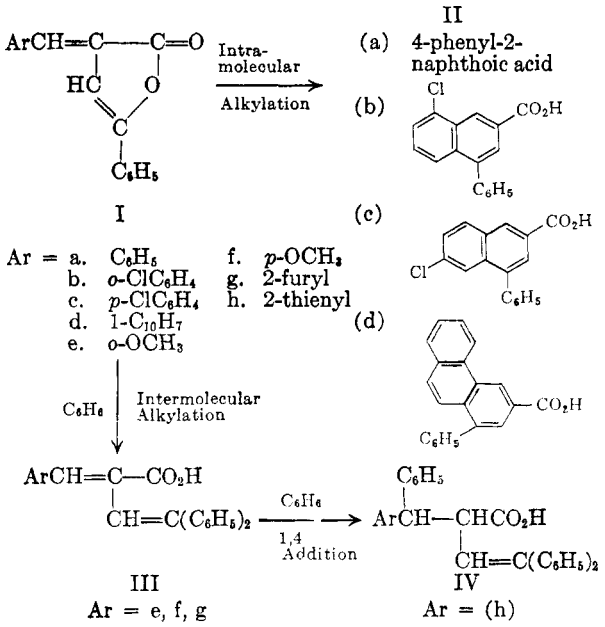
(15) J. F. Eijkman, *Chem. Weekblad*, **1**, 421 (1904); **2**, 229 (1905); **4**, 191 (1907); **4**, 727 (1907).

with γ-lactones of aliphatic hydroxy acids, which form aralkyl acids.

In the latter mode of reaction, the normal activating influence of the ether groups, which otherwise would have enhanced intramolecular attack by over-all electron release, was destroyed by coordination of the electron pairs on oxygen with the Lewis acid catalyst. The resulting preferential electrophilic attack on benzene is therefore not unexpected.

When 2-thienylidene replaced benzylidene, intermolecular alkylation was followed by 1,4-addition of the elements of benzene to the conjugated carbonyl system to form 1,1,4-triphenyl-4-(2′-thienyl)-1-butene-3-carboxylic acid (IV. Ar = ) in 91% yield.

The *m*- and *p*-nitrobenzylidenebutenolides failed to react under any of the conditions employed.



The structures of the three types of products were established by analytical data, infrared, and ultraviolet spectral evidence, and in types II and III, by decarboxylation to the parent hydrocarbons, several of which are also new compounds (see Experimental).

Although these lactones bear a formal structural resemblance to cyclic anhydrides, there was no evidence of any acylation products (either intra- or intermolecular) which one would obtain with anhydrides under these conditions. The structurally similar azlactones, however, do give some acylated products under comparable conditions.[16,17]

Variations in catalyst, temperature, and solvents were also examined. Boron trifluoride etherate and stannic chloride were substituted for aluminum chloride, but both proved ineffective even at a reaction temperature of 80°. Increased temperature was deleterious, for, in refluxing benzene, using aluminum chloride, the yield of IIa was markedly reduced to 15%.

The influence of solvent on the conversion of Ia to IIa is summarized in Table I. Solvent participation was observed only with chlorobenzene. A mixture was obtained, from which a product, believed to be 4-(*p*-chlorophenyl)-2-naphthoic acid, was isolated.

TABLE I. EFFECT OF SOLVENT ON INTRAMOLECULAR ALKYLATION REACTION AT 25°

Solvent	Yield, 4-phenyl-2-naphthoic acid, %
Benzene	70
Toluene	70
Dichloromethane	49
Tetrachloroethane	26
Nitrobenzene	0
Carbon disulfide	0
Carbon tetrachloride	0
Anisole	0

Experimental

Only typical syntheses are described to illustrate the general methods employed. Yields, melting points and analytical data for the materials prepared are summarized immediately following the procedures.

All melting points are corrected and were obtained using a total immersion thermometer in an oil bath. Initial uncorrected melting points were determined on a Fisher–Johns block. Potassium bromide pellets were used, except where noted, to obtain infrared spectra. A Perkin–Elmer spectrometer, Model 21, was used for this purpose. Ultraviolet spectra were measured in 95% ethanol using a Beckman DK-2 spectrophotometer. The elemental analyses were carried out by Micro-Tech Laboratories, Skokie, Illinois.

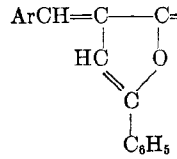
Preparation of α-Arylidene-γ-phenyl-Δ$^{\beta,\gamma}$-butenolides.—In a 200-ml. three-necked, round-bottom flask fitted with a gas inlet tube, thermometer, and a reflux condenser equipped with a drying tube were placed 0.10 mole of 3-benzoylpropionic acid,[18] 0.10 mole of the respective aldehyde, 0.10 mole of freshly fused anhydrous sodium acetate, and 0.60 mole of acetic anhydride. The flask was heated at 100° (water bath) for 2 hr. while the solution was saturated with dry, oxygen-free nitrogen. At the end of this time, the colored solution was allowed to cool and the gas inlet tube removed. Upon solidification, small amounts of 70–80% aqueous ethanol were added until a slurry formed. The slurry was transferred to a beaker and the volume of added aqueous ethanol was brought to 200 ml. The resulting colored suspension was stirred thoroughly with a glass rod before collecting the solid on a Büchner funnel. The filter cake was washed with small amounts of cold aqueous ethanol, then several times with hot water. After crystallization from aqueous ethanol, the lactone was thoroughly dried. (See Table II.)

Condensation Reactions Attempted.—Attempts were made to condense 3-benzoylpropionic acid with the following carbonyl compounds: crotonaldehyde, acetophenone, 2-pyridinecarboxaldehyde, and indole - 3 - carboxaldehyde. The respective γ-lactones could not be isolated.

Reaction of Butenolides with Benzene under Friedel–Crafts Conditions. General Method.—Anhydrous alumi-

(16) W. I. Awad and M. S. Hafez, *J. Org. Chem.*, **26**, 2055 (1961).
(17) R. Filler and Y. S. Rao, *ibid.*, **27**, 2403 (1962).
(18) Aldrich Chemical Co., Milwaukee, Wis.

TABLE II. α-ARYLIDENE-γ-PHENYL-$\Delta^{\beta,\gamma}$-BUTENOLIDES[g]



Ar	Yield, %	M.p.	Reported m.p.	Infrared spectral data (lactone >C=O)
C_6H_5	52	150.8–151.6°	155°[a]	1785 cm.$^{-1}$(s); 1790 cm.$^{-1}$(in CCl_4)
o-ClC_6H_4	52	162–162.4°	164°[a]	1785 cm.$^{-1}$(s)
o-$CH_3OC_6H_4$	57	155.9–156.6°	...	1760 cm.$^{-1}$(s)
m-$NO_2C_6H_4$	71	215.6–216.4°[a]	204–205°[c]	1760 cm.$^{-1}$(s)
p-ClC_6H_4	44	228.4–229.2°	...	1765 cm.$^{-1}$(s)
p-$CH_3O\,C_6H_4$	51	170.2–170.6°	168–169°[d]	1655 cm.$^{-1}$(s)
p-$NO_2C_6H_4$	67	295°	295°[e]	1765 cm.$^{-1}$(s)
1-$C_{10}H_7$	32	157.6–158.1°	...	1765 cm.$^{-1}$
C_6H_5CH=CH—	48	163.6–164.6°	154°[e]	1750 cm.$^{-1}$
2-Furylidene	48	118.8–119.3°	116°[e]	1760 cm.$^{-1}$
2-Thienylidene	37	146.2–146.8°[f]	...	1760 cm.$^{-1}$

[a] F. W. Schueler and C. Hanna, *J. Am. Chem. Soc.*, **73**, 3528 (1951). [b] Calcd. for $C_{17}H_{11}NO_4$: C, 69.62; H, 3.78. Found: C, 69.70; H, 3.97. [c] See ref. 7. [d] See ref. 6. [e] See ref. *a*. [f] Calcd. for $C_{27}H_{22}SO_2$: C, 70.84; H, 3.96. Found: C, 70.95; H, 4.21. [g] Recrystallization solvent: aqueous ethanol.

num chloride (0.09 mole) and 125 ml. of dry, thiophene-free benzene were placed in a 1-l., three-necked, round-bottomed flask, fitted with a stirrer, thermometer, and adapter to which was attached a dropping funnel and a drying tube atop a condenser. The temperature was lowered and maintained at 10–15° for 1 hr. while the mixture was stirred moderately. The dry butenolide (0.03 mole), in a solution or slurry with 125 ml. of dry benzene, was added at 10–15° with vigorous stirring. A fluorescent colored solution, normally orange, was formed on initial addition of the butenolide. Addition of the reagents was completed in 10 to 20 min. and then the temperature of the mixture was allowed to rise to room temperature. Vigorous stirring was continued for 3 hr., except where noted. During this period the solution normally became translucent. This was usually a visual indication that a reaction had occurred. The complex was decomposed by the slow addition of about 60 ml. of 15% hydrochloric acid and the resulting mixture extracted with ether. The organic layer was washed with water until neutral to litmus. After drying over calcium chloride, the solution was filtered and the solvent removed by distillation until a solid separated. On cooling and filtering, white crystals were obtained. Some of these materials were difficult to dissolve, and a satisfactory method of recrystallization could not be found. However, the material was further purified by dissolving in large volumes of ethanol–water. *Note:* Besides using the visual method to determine that a reaction had occurred, small amounts of the reaction mixture were extracted and acidified. A white precipitate confirmed that reaction had occurred while a yellow precipitate indicated negative results.

Intramolecular Alkylation Reactions.—α-Benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide gave 4-phenyl-2-naphthoic acid, 70–75% crude yield, cryst. (ethanol–water), yield 60–70%, white needles, m.p. (uncorr.) 262–263°. Mol. wt., calcd: 248. Found: 248 (neut. equiv.). λ_{max}^{EtOH} 239 mμ (ε 62,400), 290 mμ (ε 8,500), 327 mμ (ε 2,900). Infrared absorption at 1685 cm.$^{-1}$ ($CHCl_3$, 1695 cm.$^{-1}$).

α-(o-Chlorobenzylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide gave 4-phenyl-8-chloro-2-naphthoic acid, 99% crude, cryst. (ethanol–water), yield 82%, white needles, m.p. 252.8–253.4°.

Anal. Calcd. for $C_{17}H_{11}O_2Cl$: C, 72.29; H, 3.92. Found: C, 72.11; H, 4.17. Mol. wt. calcd: 282. Found: 282 (neut. equiv.). λ_{max}^{EtOH} 239 mμ (ε 57,300), 302 mμ (ε 8,500); infrared absorption at 1695 cm.$^{-1}$(s).

α-(p-Chlorobenzylidene)-α-phenyl-$\Delta^{\beta,\gamma}$-butenolide gave 4-phenyl-6-chloro-2-naphthoic acid, 94% crude, cryst. (ethanol–water), yield 31%, white needles, m.p. 313.2–314.4°.

Anal. Calcd. for $C_{17}H_{11}O_2Cl$: C, 72.29; H, 3.92. Found: C, 72.48; H, 4.12. Mol. wt. calcd: 282. Found: 282 (neut. equiv.). λ_{max}^{EtOH} 242 mμ (ε 22,300), 295 mμ (ε 6,000), and 339 mμ (ε 2,500); infrared absorption at 1695 cm.$^{-1}$(s).

α-(1-Naphthylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide was converted to 4-phenyl-2-carboxyphenanthrene, 31% crude, plus a large amount of resin, cryst. (ethanol–water), yield 21%, cream-colored amorphous structure, m.p. 286.8–287.6°.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.19; H, 4.82. Mol. wt., calcd: 298. Found: 301 (neut. equiv.). λ_{max}^{EtOH} 223 mμ (ε 33,500), 263 mμ (ε 38,300), and 312 mμ (ε 12,600); infrared absorption at 1685 cm.$^{-1}$(s).

Intermolecular Alkylation Reactions.—α-(o-Methoxybenzylidene) - γ - phenyl-$\Delta^{\beta,\gamma}$ - butenolide gave 1,1-diphenyl-4-(o-methoxyphenyl)-1,3-butadiene-3-carboxylic acid, 81% crude, cryst. (ethanol–water), white needles, m.p. 309.0–313.4°. Satisfactory method of recrystallization could not be found.

Anal. Calcd. for $C_{24}H_{20}O_3$; C, 80.88; H, 5.66. Found: C, 81.04; H, 5.70. Mol. wt., calcd.: 356. Found: 372 (neut. equiv.), attributed to extremely poor solubility in solvent. λ_{max}^{EtOH} 237 mμ (ε 13,800), 265 mμ (ε 4,100), 271 mμ (ε 4,900), and 314 mμ (ε 11,000); infrared absorption 1680 cm.$^{-1}$(s).

α-(p-Methoxybenzylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide formed 1,1-diphenyl-4-(p-methoxyphenyl)-1,3-butadiene-3-carboxylic acid, 91% crude, cryst. (ethanol–water), yield 52%, white needles, m.p. 265.8–266.4°.

Anal. Calcd. for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 81.17; H, 6.01. Mol. wt., calcd: 356. Found: 360 (neut. equiv.). λ_{max}^{EtOH} 305 mμ (ε 17,600), 264 mμ (ε 5,600), and 271 mμ (ε 5,600); infrared absorption at 1665 cm.$^{-1}$(s).

α-(Cinnamylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide reacted to yield a compound, possibly 1,1,6-triphenyl-1,3-hexadiene-3-carboxylic acid, 88% crude, cryst. (ethanol–water), yield 69%, white needles, m.p. 237.0–237.6°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.74; H, 6.21. Found: C, 85.07; H, 5.09. Mol. wt., calcd: 354. Found: 356 (neut. equiv.). λ_{max}^{EtOH} 260 mμ (ε 1,700), 264 mμ (ε 1,500), 266 mμ (ε 1,600) and 273 mμ (ε 1,300); infrared absorption 1685 cm^{-1}(s).

α-(2-Furylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide gave 1,1-diphenyl-4-(2′-furyl)-1,3-butadiene-3-carboxylic acid, 96% crude, plus a trace amount of a red-colored material, cryst.

(ethanol–water), yield 68%, white needles, m.p. 237.6–238.0°.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.91; H, 5.17. Mol. wt., calcd: 316. Found: 319 (neut. equiv.). λ_{max}^{EtOH} 263 mμ (ε 2,200), 270 mμ (ε 2,000) and 322 mμ (ε 12,500); infrared absorption at 1675 cm.$^{-1}$(s).

Intermolecular Alkylation and Addition.—α-(2-Thienylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide formed 1,1,4-triphenyl-4-(2′-thienyl)-1-butene-3-carboxylic acid, 94% crude yield, cryst. (ethanol–water), yield 91%, white needles, m.p. 268.6–269.6°.

Anal. Calcd. for $C_{27}H_{22}O_2S$: C, 78.98; H, 5.41. Found: C, 78.79; H, 5.54. Mol. wt., calcd: 410. Found: 410 (neut. equiv.). Sulfur tests positive. λ_{max}^{EtOH} 241 mμ (ε 10,600) and 270 mμ (ε 800); infrared absorption at 1710 cm.$^{-1}$(s).

Attempted Alkylations.—α-(*m*-Nitrobenzylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide failed to give a reaction after 4 hr. α-(*p*-Nitrobenzylidene)-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide also failed to react after 4.5 hr., as determined by mixed melting points and comparison of infrared spectra.

Decarboxylation. General Method.—In a 20-ml. round-bottomed distillation flask, fitted with thermometer and condenser, were placed 0.017 mole of carboxylic acid and 0.0014 mole of copper chromite in 10 ml. of quinoline. The mixture was heated under slow reflux for 24 hr. The mixture was transferred to a beaker and diluted with 100–150 ml. of ether. The organic layer was washed with several portions of 15% hydrochloric acid, then 5% sodium bicarbonate and water until neutral to litmus. The organic layer was dried over anhydrous calcium chloride. After filtering, the ether was removed by distillation to yield the product.

4-Phenyl-8-chloro-2-naphthoic acid gave 1-phenyl-5-chloronaphthalene, cryst. (ethanol–water), white needles, m.p. 43.2–43.6°.

Anal. Calcd. for $C_{16}H_{11}Cl$: C, 80.50; H, 4.64. Found: C, 80.40; H, 4.57. λ_{max}^{EtOH} 229 mμ (ε 97,000) and 295 mμ (ε 17,000).

4-Phenyl-6-chloro-2-naphthoic acid yielded 1-phenyl-7-chloronaphthalene, cryst. (ethanol–water), white needles, b.p. (uncorr.) 148–150°/3.5 mm., m.p. 78.0–78.6° (lit.,[19] 77–78°). λ_{max}^{EtOH} 220 mμ (ε 44,000), 265 mμ (ε 58,000), and 299 mμ (ε 17,000).

4-Phenylphenanthrene-2-carboxylic acid formed 4-phenylphenanthrene, cryst. (ethanol–water), white, amorphous structure, m.p. 78.0–78.8° (lit.,[20] 80–81°). λ_{max}^{EtOH} 298 mμ (ε 18,760) and 288 mμ (ε 15,870).

(19) F. G. Baddar, L. S. El-Assal, and N. A. Doss *J. Chem. Soc.*, 1027 (1959).

1,1-Diphenyl-4-(*o*-methoxyphenyl)-1,3-butadiene-3-carboxylic acid yielded 1,1-diphenyl-4-(*o*-methoxyphenyl)-1,3-butadiene, cryst. (methanol–water), white needles, m.p. (uncorr.) 123–124°.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 87.49; H, 6.57. λ_{max}^{MeOH} 240 mμ (ε 15,100), 262 mμ (ε 7,040), 269 mμ (ε 6,970), 320 mμ (ε 4,580), and 313 mμ (ε 4,190).

Catalyst and Temperature Study with Compound Ia.—a. With aluminum chloride at 80°. This was carried out under the conditions described previously. 4-Phenyl-2-naphthoic acid (15%), m.p. (uncorr.) and mixed m.p. (uncorr.) 260–262°, was isolated, plus an unidentified red colored product (*ca.* 5%). The remaining portion was a brown colored tar-like material. b. With stannic chloride at 25°. Starting material (90%), m.p. (uncorr.) and mixed m.p. (uncorr.) 147–152°, was recovered. c. With stannic chloride at 80°. Only starting material was isolated. d. With boron trifluoride etherate at 25°. Starting material (93%) was recovered. e. With boron trifluoride at 80°. Only starting material was isolated.

Solvent Study.—All reactions were conducted at room temperature, using anhydrous aluminum chloride. a. Using toluene, a crude product, (70%) m.p. (uncorr.) 260–261° was obtained. The mixed m.p. (262–264°) and its infrared spectrum showed that the material was 4-phenyl-2-naphthoic acid. b. Using chlorobenzene, a crude product, m.p. (uncorr.) 186–193° was isolated. Cryst. (ethanol–water), yielded 4-(*p*-chlorophenyl)-2-naphthoic acid, white needles, m.p. 279.1–281.0°. Qualitative analysis for halogen showed presence of chlorine.

Anal. Calcd. for $C_{17}H_{11}O_2Cl$: C, 72.29; H, 3.92. Found: C, 73.14; H, 4.08. Mol. wt., calcd: 282. Found: 284 (neut. equiv.). λ_{max}^{EtOH} 236 mμ (ε 80,200) and 293 mμ (ε 12,000); infrared absorption at 1685 cm.$^{-1}$.

c. Using nitrobenzene, only starting material was isolated (70%). d. Using anisole, only starting material was isolated (90%). e. Using carbon disulfide, starting material was isolated (82%). f. Using carbon tetrachloride, starting material was recovered (80%). g. Using methylene chloride, a white material was obtained which was difficult to separate by the normal procedure. The product was 4-phenyl-2-naphthoic acid (49%), m.p. and mixed m.p. (uncor.) 260–263°; infrared carbonyl absorption at 1685 cm.$^{-1}$. h. Using tetrachloroethane, a white product, identified as 4-phenyl-2-naphthoic acid, was obtained, 26%, m.p. and mixed m.p. (uncorr.) 260–264°; infrared carbonyl absorption at 1685 cm.$^{-1}$.

(20) A. D. Campbell, *ibid.*, 3659 (1954).