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AN ABSTRACT OF THE THESIS OF

Clark Keelock Chow for the M.S. in Chemistry
(Name) (Degree) (Major)

Date thesis is presented: June 5, 1969.

Title: Cyclization Studies Involving the Synthesis of 5-Substituted-
1-naphthol.

Abstract approved:

(Major Professor)

The γ -o-substituted-phenylparaconic acids were prepared by a method patterned after that of Fuson. These paraconic acids were prepared in good yield. A re-investigation of the Perkin and Fittig methods of preparing γ -phenylisocrotonic acid was carried out without success.

The synthesis of γ -o-halophenylisocrotonic acids by thermal, and catalyzed decarboxylation of γ -o-halophenylparaconic acid, have been carried out in good yield. An effective catalyst, optimum temperature and reaction period of decarboxylation of the γ -o-halophenylparaconic acids have been determined. Infrared absorptions have characterized the γ -o-halophenylisocrotonic acids formed to be in the stable trans form.

Cyclization of γ -o-halophenylisocrotonic acids was accomplished by isomerization of the trans acid to cis acid by ultra-violet irra-

diation, followed by refluxing in the presence of sodium acetate and acetic anhydride. The subsequent hydrolysis of the acetylated-naphthol afforded the 5-halo-1-naphthol.

**CYCLIZATION STUDIES INVOLVING THE
SYNTHESIS OF 5-SUBSTITUTED-1-NAPHTHOL**

by

CLARK KEELOCK CHOW

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

Portland State University

1969

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This Thesis is dedicated to
my Grandmother
Chan Su-Ying

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I. INTRODUCTION

The purpose of this research was to carry out the synthesis of 5-substituted-1-naphthols via a method involving cyclization of the intermediate, γ -o-substituted-phenylisocrotonic acid. In particular it was necessary that 5-nitro-1-naphthol be prepared since this compound was required in the further study of the oxidative ring cleavage of substituted-nitronaphthalenes.

Some of these substituted-naphthols have been prepared by other methods which are time consuming, tedious, or inadequate in terms of yields.

The synthesis of the substituted naphthols involved three steps which are shown in the following schematic series:

The o-substituted-benzaldehyde was converted to the γ -o-substituted-phenylparaconic acid which in turn was heated or treated with a catalyst. The latter operation permitted the decarboxylation of the γ -o-substituted-phenylparaconic acid and the subsequent formation of the γ -o-substituted-phenylisocrotonic acid. The γ -o-substituted-phenylisocrotonic acid was cyclized to an acetyl derivative which was easily hydrolyzed to the desired naphthol.

II. HISTORICAL

The historical section will be discussed under the following headings: (a) Preparation of γ -o, or p-substituted-phenylparaconic acids and γ -o, or p-substituted-phenylisocrotonic acids. (b) Preparation of 5- and 7-halo-1-naphthols.

Preparation of γ -o, or p-substituted-phenylparaconic Acids and γ -o, or p-substituted-phenylisocrotonic Acids.

The synthesis of cinnamic acid and its analogs by the interaction of an aromatic aldehyde with an acid anhydride in the presence of a salt of an acid was first reported by Perkin in 1868 (1).

In 1883, Fittig and Jayne (2) found that if benzaldehyde was allowed to react with succinic anhydride and sodium succinate at 100°C, the product was γ -phenylparaconic acid. Furthermore, they observed that on heating γ -phenylparaconic acid, carbon dioxide was lost and the β , γ -unsaturated acid, γ -phenylisocrotonic acid was formed.

The latter compound was also reported by Perkin when the above reaction was conducted at 150°C (3,4).

The synthesis of γ -o, and p-chlorophenylparaconic acid was reported by Erdmann (5) in 1888 by the condensation of o or p-chlorobenzaldehyde, succinic anhydride and sodium acetate. The distillation of γ -o or p-chlorophenylparaconic acid yielded γ -o, or p-chlorophenylisocrotonic acids, respectively (6).

Patterned after the method of Erdmann (5), Fuson (7) in 1924 was able to prepare the γ -o-bromophenylparaconic acid in 50% yield. A year later, Fuson (8) reported the synthesis of γ -m-bromophenylparaconic acid in 20% yield as well as the γ -p-bromophenylparaconic acid.

The synthesis of γ -p-nitro-phenylparaconic acid was carried out by A. Angeletti in 1929 (9). The γ -o-nitrophenylisocrotonic acid was reported in 1934 by F. Schenck (10). The synthesis of the latter involved the condensation of α -(o-nitrophenyl)acetaldehyde and malonic acid.

A modification of the Reformatsky Reaction by Miller and Nord (11) in 1951, enabled these investigators to prepare the γ -phenylisocrotonic acid in 34% yield.

An excellent paper on the re-investigation of the reaction of the sodium succinate with some aromatic aldehydes was published in 1960, by G. M. Anteunis (12). A new technique was described by this investigator which increased the yield of the γ -phenylparaconic acid to 85%. He also found that it was better to prepare γ -phenylparaconic acid first, and then convert it into γ -phenylisocrotonic acid in a separate step, rather than to carry out the preparation of the γ -phenylisocrotonic acid directly by allowing sodium succinate and benzaldehyde to react at a higher temperature.

In 1964, Oda, Kawabata, and Tanimoto (13) were able to obtain γ -p-chlorophenylisocrotonic acid in 55% yield via the reaction of p-chlorobenzaldehyde, and the ylide (14), $\phi_3\text{P}=\text{CHCH}_2\text{C}(=\text{O})\text{OEt}$.

Preparation of 5- and 7-halo-1-naphthols.

The earliest report of the synthesis of 5- or 7-halo-1-naphthol was by Erdmann and Kirchhoff (15) in 1888. They demonstrated that on heating o-, or p-chlorophenylparaconic acid rapidly to a higher temperature, 5- or 7-chloro-1-naphthol was prepared.

In 1949, Louis Fieser (16) prepared p-chlorophenylparaconic

acid according to the method of Erdmann, et. al. Distillation of the crude product resulted in a 22% yield of 7-chloro-1-naphthol.

A rather interesting method was employed by Beech and Legg (17) in the synthesis of 7-chloro-1-naphthol. They were able to convert 8-nitro-2-aminonaphthalene to 7-chloro-1-nitronaphthalene via the Sandmeyer Reaction and then to the naphthol compound by reduction of the nitro compound, followed by diazotization of the aminonaphthalene.

A. P. Luric, et al (18) described the synthesis of 5-chloro-1-naphthol from 5-amino-1-naphthol using the Sandmeyer Reaction. The yield of the desired naphthol was about 8%.

In 1959, Franzen (19) demonstrated that 7-chloro-1-naphthol could be prepared by the cyclization of a γ -p-chlorophenylbutyric acid to the 7-halo-1-tetralone, followed by bromination and dehydrobromination of the intermediate.

Vorozhtov and Lisitsyn (20) in 1960, published a report which indicated that 5-chloro-1-naphthol was obtained in 82% yield by heating 1,5-dichloronaphthalene with powdered sodium hydroxide and copper powder in methanol.

In 1961, El-Abbady, et al (21) described the preparation of 5-chloro-1-naphthol via the Stobbe condensation. It involved the reaction of *o*-chlorobenzaldehyde and methylsuccinate in *t*-butyl alcohol and potassium *t*-butoxide to give methyl hydrogen *cis* γ -*o*-chlorophenylitaconate. The latter compound was then treated with sodium acetate and acetic anhydride to give methyl 4-acetoxy-8-chloro-2-naphthoate (22). Subsequent hydrolysis, methylation, decarboxylation, and demethylation afforded 5-chloro-1-naphthol (23). The 7-chloro-1-naphthol was also made starting, with the *p*-chlorobenzaldehyde.

The compound, 5-bromo-1-naphthol was prepared by Fuson (7) in 1924 by the method of Erdmann, which involved the heating of γ -o-bromophenylparaconic acid rapidly to a high temperature. He also announced the preparation of the same naphthol by a different procedure as illustrated below (24,25):

Hill and Short (26) also described a method for the preparation of 5-bromo-1-naphthol involving the bromination of 1-nitronaphthalene, reduction of the nitro compound to 5-bromo-1-aminonaphthalene, diazotization of the amino compound and thence to the product in 41% yield.

An elegant paper on the synthesis of α , or β -fluoronaphthalene derivatives is that of Adcock and Dewar (27). These investigators reported that 7-fluoro-1-naphthol could be prepared by the following route (28,29):

The 5-iodo-1-naphthol was synthesized by Scholl and Seer (30), in 1922, according to the following schematic series:

III. DISCUSSION

The data is discussed in three sections as a matter of convenience. The first section is considered under the general heading, Preparation of paraconic acids; the second, Decarboxylation; and the third, Cyclization.

Preparation of paraconic acids.

It had been reported by Fittig and Jayne that γ -phenylisocrotonic acid could be prepared exclusively if benzaldehyde and succinic anhydride were allowed to react at 170°C. Therefore, it was decided initially to carry out the condensation of o-chlorobenzaldehyde and succinic anhydride at the higher temperature with the intention of isolating γ -o-chlorophenylisocrotonic acid directly. Instead of the expected product, only a tarry material was obtained, from which no γ -o-chlorophenylisocrotonic acid could be isolated. In another run, this time with o-bromobenzaldehyde, the results again were negative. It therefore became necessary to prepare the γ -o-substituted-phenylparaconic acid first and then convert it in a separate step into the γ -o-substituted-phenylisocrotinic acid as had been suggested by Anteunis (12).

The synthesis of γ -o-substituted-phenylparaconic acid was accomplished as illustrated in the following schematic series:

The procedure followed was essentially that of C. Fuson (7) with slight modification. The data is shown in Table I.

TABLE I

<u>Product</u>	<u>Temperature</u>	<u>Time</u>	<u>Yield</u>
γ - <u>o</u> -Fluorophenyl- paraconic acid	140°, 120°	3 hrs.	62.0%
		6 hrs.	41.0%
γ - <u>o</u> -Chlorophenyl- paraconic acid	140°, 120°	3 hrs.	81.2%
γ - <u>o</u> -Bromophenyl- paraconic acid	140°, 120°	5 hrs.	64.2%
		3 hrs.	75.3%
γ - <u>o</u> -Iodophenyl- paraconic acid	140°, 120°	5 hrs.	74.4%
γ - <u>o</u> -Nitrophenyl- paraconic acid	140°, 120°	3 hrs.	38.3%

The reaction between o-fluorobenzaldehyde or o-nitrobenzaldehyde and succinic anhydride took place quite rapidly at 140°C. However, this was not the case with the o-chlorobenzaldehyde, o-bromobenzaldehyde, or o-iodobenzaldehyde. Nevertheless, analogous results were obtained in all paraconic acids synthesis.

In the preparation of each paraconic acid, an intractable tar was obtained as a by-product. No attempt was made to isolate or identify any product from the resinous material.

As the reaction time was reduced from either six or five hours to three hours in the synthesis of γ -o-fluoro or γ -o-bromophenylparaconic acid, the yield was increased. In the case of the γ -o-nitrophenylparaconic acid, the yield was rather mediocre even at the three hour period. No additional experiments were conducted to determine if the reaction time could be shortened to improve the yield.

One may interpret the difference in yields between the γ -o-halophenylparaconic acid, and γ -o-nitrophenylparaconic acid as due to steric effects (31). The steric effects decrease in the order NO_2 , I, Br, Cl, and F. Therefore, the nitro substituent would offer the most steric strain or steric hindrance which may account for the lower yield.

Decarboxylation of γ -o-substituted-phenylparaconic acid.

Paraconic acids are known to be susceptible to decarboxylation (32). Fittig (33) had reported the thermal decarboxylation of phenylparaconic acid produced γ -phenylbutyrolactone, γ -phenylisocrotonic acid and also a small amount of allylbenzene. When γ -o-chlorophenylparaconic acid was subjected to a thermal decarboxylation at 150° for half an hour, no observable reaction occurred. When γ -o-chlorophenylparaconic acid was heated at a higher temperature, $205^\circ \pm 5^\circ$, for a period of two and one-half hours under a nitrogen atmosphere, a 6% yield of γ -o-chlorophenylisocrotonic acid was obtained along with

42% recovery of the starting material. Distillation of γ -o-chlorophenylparaconic acid under nitrogen atmosphere at 270-280° caused extensive carbonization; γ -o-chlorophenylisocrotonic acid was not isolated.

Attempted decarboxylation of γ -o-chlorophenylparaconic acid employing either copper powder alone or copper powder in quinoline did not give an effective reaction; only a trace of γ -o-chlorophenylisocrotonic acid was detected.

TABLE II
Decarboxylation of γ -o-Chlorophenylparaconic Acid

<u>Temperature</u>	<u>Time</u>	<u>Catalyst</u>	<u>Condition</u>	<u>γ-<u>o</u>-Chlorophenylisocrotonic acid</u>	<u>Residue</u>
150°	30 min.	---	---	---	Starting material
186 $\pm$ 3°	180 min.	---	---	4%	57% Starting material
205 $\pm$ 5°	150 min.	---	N ₂	5%	42% Starting material
235 $\pm$ 5°	150 min.	Cu	N ₂	---	?
230°	180 min.	Cu	N ₂	trace	?
270-280°	40 min.	---	N ₂	---	?

Refluxing γ -o-chlorophenylparaconic acid in a high boiling solvent 2,2' oxydiethanol (B.P. 245°) caused decarboxylation with the resulting formation of γ -o-chlorophenylbutyrolactone. γ -Lactone was formed via lactonization of β , γ -unsaturated acid through action of mineral acid or heat (34). The equilibrium between the β , γ -un-

saturated acid and γ -lactone has been termed by Linstead a "lacto-enoic tautomerism" (35). In 1959, Johnson and Petersen (36), reported the formation of an β , γ -unsaturated acid and γ -lactone via decarboxylation of itaconic acid. They found that the lactone was in a greater concentration before equilibrium was reached. This observation suggested that the lactone was the primary product of the decarboxylation step, and the unsaturated acid was formed via the lacto-enoic tautomerism.

γ -o-Chlorophenylparaconic acid was decarboxylated at 210° ; subsequent hydrolysis of the proposed intermediate γ -o-chlorophenylbutyrolactone, and dehydration by sulfuric acid resulted only in γ -o-chlorophenylbutyrolactone instead of the γ -o-chlorophenylisocrotonic acid.

The above observation was contrary to the early premise by Johnson and Petersen (36); however, it is in complete agreement with the latter work of Johnson and Hunt (37).

The formation of γ -lactone is dependent upon the extent of heat treatment. Upon rapid distillation, the unsaturated acid is formed in higher yield. The unsaturated acid derivative of γ , γ -disubstituted-paraconic acid readily undergoes lactonization upon heating at the boiling point, while the unsaturated acid derivative of γ -monosubstituted-paraconic acid can be distilled without isomerisation to the

lactones (38). γ -Lactone are not generally isomerized to the unsaturated acid (34, 35). When γ -o-chlorophenylisocrotonic acid was treated at room temperature with concentrated sulfuric acid for twenty minutes, γ -o-chlorophenylbutyrolactone was not found in the reaction mixture.

However, when γ -o-chlorophenylisocrotonic acid and γ -o-bromophenylisocrotonic acid were refluxed with dilute sulfuric acid for 2 hours, the γ -o-bromophenylbutyrolactone was obtained in 35% yield, and only a trace amount of γ -o-chlorophenylbutyrolactone was isolated.

γ, γ -diphenylisocrotonic acid was isomerized to γ, γ -diphenylbutyrolactone in the presence of cold concentrated sulfuric acid at room temperature within fifteen minutes. This observation is in accordance with the fact that the γ -substituted β, γ -unsaturated acid does not isomerize to γ -lactone as easily as the γ, γ -disubstituted β, γ -unsaturated acid. The inert behavior of the γ -o-halophenylisocrotonic acid towards lactonization suggested that the inductomeric effect and electromeric effect probably stabilizes the β, γ -unsaturated acid.

TABLE III
Thermal Decarboxylation of γ -o-Chlorophenylparaconic Acid

<u>Temperature</u>	<u>Time</u>	<u>γ-<u>o</u>-Chlorophenyl- isocrotonic acid</u>	<u>5-Chloro- naphthol</u>
220°	168 min.	67%	---
230°	130 min.	68.02%	4.09%
240°	122 min.	63.8%	8.7%

TABLE IV
Acid-catalyzed Decarboxylation of γ -o-Chlorophenylparaconic
Acid by KHSO_4

<u>Temperature</u>	<u>Time</u>	<u>γ-<u>o</u>-Chlorophenyl- isocrotonic acid</u>	<u>5-Chloro- naphthol</u>
220°	86 min.	70.8%	6.9%
230°	71 min.	71.0%	8.1%
240°	70 min.	69.8%	8.1%
250°	64 min.	68.9%	7.04%
260°	74 min.	53.0%	4.5%
230-310° *	21 min.	11.6%	36%

* γ -o-Chlorophenylparaconic acid was distilled at reduced pressure with a rapid increase in temperature.

Decarboxylation of γ -o-chlorophenylparaconic acid was carried out under, both, thermal and acid-catalyzed thermal conditions at various temperatures as shown in Table III and Table IV. The experimental results demonstrated that an acid catalyzed reaction reduced the decarboxylation time by one-half as compared to the thermal decarboxylation at the same temperature. Decarboxylation by potassium hydrogen sulfate was accompanied by a more vigorous evolution of gas, and provided for purer products. Thermal decarboxylation required a longer reaction period which could conceivably lead to a competing side reaction i.e. decarboxylation of β , γ -unsaturated acid. No attempt was made to identify the presence of o-chloroallylbenzene as reported by Fittig.

Decarboxylation of γ -o-bromophenylparaconic acid showed analo-

gous results as the γ -o-chlorophenylparaconic acid. The lower yield in the first run of Table V can be attributed to some of the β , γ -unsaturated acid cyclizing to 5-bromo-1-naphthol.

TABLE V

Acid-catalyzed Decarboxylation of γ -o-Bromophenylparaconic Acid
by KHSO_4

<u>Temperature</u>	<u>Time</u>	<u>Catalyst</u>	<u>Yield</u>
230° *	80 min.	KHSO_4	47.5%
225°	110 min.	KHSO_4	77.5%
230°	105 min.	KHSO_4	75%

* U.V. irradiation was applied 30 min. before vacuum distillation, 14.5% of 5-bromo-1-naphthol was also obtained.

Acid-catalyzed decarboxylations of γ -o-fluoro and γ -o-iodo-phenylparaconic were favored by shorter reaction periods. The reactions occurred instantly with a rapid evolution of carbon dioxide. Prolonged heating resulted in decomposition, as indicated by the occurrence of iodine vapors, and charring of γ -o-fluorophenylparaconic acid.

TABLE VI

Acid-catalyzed Decarboxylation of γ -o-Fluorophenylparaconic
Acid by KHSO_4

<u>Temperature</u>	<u>Time</u>	<u>Yield</u>
230° *	90 min.	57%
230°	68 min.	77%
235°	71 min.	66.4%
230 $\pm$ 10°	73 min.	66%

* The reactant turned dark brown, indicating carbonization occurred.

TABLE VII

Acid-catalyzed Decarboxylation of γ -o-Iodophenylparaconic
Acid by KHSO_4

<u>Temperature</u>	<u>Time</u>	<u>Yield</u>
230°	75 min.	58.8%
230° **	89 min.	37.7%
220 $\pm$ 5° **	--- ?	40.8%
225 $\pm$ 3°	65 min.	74.0%

** γ -o-Iodophenylparaconic acid began to decompose, iodine vapor was detected in the reaction vessel.

When γ -o-nitrophenylparaconic acid was subjected to decarboxylation conditions, carbonization occurred immediately at temperature above its melting point. This was first observed when the melting

point of γ -o-nitrophenylparaconic acid was determined. Bubbles of gas occurred in the capillary tube and the γ -o-nitrophenylparaconic acid turned into a dark brown oil. Decarboxylation of γ -o-nitrophenylparaconic acid was attempted under a nitrogen atmosphere with a catalytic amount of potassium hydrogen sulfate at 210° . The reactant turned to a dark brown oil within five minutes after immersion in an oil bath at 210° , and vacuum distillation did not yield the expected product.

When γ -o-nitrophenylparaconic acid was refluxed in petroleum-ether (B.P. 90° - 120°) with a catalytic amount of potassium hydrogen sulfate for 2 hours under a nitrogen atmosphere, no decarboxylation was detected. The addition of a drop of concentrated sulfuric acid caused complete carbonization of the γ -o-nitrophenylparaconic acid. A possible explanation for the failure of this reaction could be due to the intensified electronic effect of the o-nitro substituent.

Two schemes for the acid catalyzed decarboxylation of paraconic acids by the potassium hydrogen sulfate have been advanced by Johnson and Hunt (37). The first scheme is referred to as the concerted process as shown in the diagram:

In scheme I, protonation of the carbonyl oxygen of the γ -lactone causes a shift of the electrons and opens the ring. The electronic effect of the ortho substituent facilitates the shift of the electrons and stabilizes the formation of carbon-carbon double bond by conjugation.

Scheme II, protonation of ester linkage oxygen results in the rupture of the lactone ring and the formation of benzylic carbonium ion. The latter favours the cleavage of the carbonyl carbon and carbon bond and the formation of β , γ -unsaturated acid.

Scheme III represents thermal decarboxylation of paraconic acid. It is believed that the protonation occurs intramolecularly as shown by the following diagram:

The transfer of a proton is extremely difficult, as shown by the bending of the C-O-H bond. This effect was indicated by the longer reaction time in purely thermal decarboxylation as compared to acid-catalyzed thermal decarboxylation.

Cyclization

A classical example of ring closure of γ -arylcrotonic acid was described by Erdmann. The cyclization of γ -o-chlorophenylisocrotonic acid was carried out initially in accordance with the method of Erdmann. The reaction involved the direct distillation of γ -o-bromophenylparaconic acid at an extremely high temperature, 280° to 320°, which formed the intermediate γ -o-bromophenylisocrotonic acid and the latter compound underwent cyclodehydration to the desired naphthol derivative. During the reaction extensive carbonization occurred; however, a 8% yield of 5-bromo-1-naphthol was obtained.

The preparation of 5-chloro-1-naphthol was carried out by the Fuson's method (7) with some modification. It involved the acid-catalyzed decarboxylation of γ -o-chlorophenylparaconic acid and the vacuum distillation of the reaction mixture at 230° to 310°. A 36% yield of the 5-chloro-1-naphthol was obtained. This modified method afforded higher yields than either the Erdmann ring closure method or method of Fuson.

The cyclization of γ -o-substituted-phenylisocrotonic acids was patterned after the method of Badder, et al (39,40), with some modification. γ -o-Substituted-phenyl β , γ -unsaturated acids having the appropriate stereochemical configuration, that is, an aryl group cis to the $-\text{CH}_2\text{CO}_2\text{H}$ group, can undergo intramolecularly cyclodehydration and enolization to give the substituted naphthols. An attempt to cyclize γ -o-chlorophenylisocrotonic acid directly by refluxing sodium acetate and acetic anhydride (39,41,42), was not successful.

Evidently the compound, γ -o-chlorophenylisocrotonic acid remained in the stable trans form.

The conversion of the trans acid to the cis isomer was accomplished by photoisomerization. γ -o-chlorophenylisocrotonic acid was irradiated with a U.V. source for half an hour while refluxing with sodium acetate and acetic anhydride. Hydrolysis of 5-chloro-1-acetoxynaphthalene gave a 62.2% yield of 5-chloro-1-naphthol. Cyclization of other γ -o-halo-phenylisocrotonic acids to 5-halo-1-naphthol can be accomplished by the same method.

TABLE VIII
Yield of 5-halo-1-naphthol

F	Cl	Br	I
46.5%	62.2%	51.1%	40.5%

The entire operation - isomerization, cyclization and hydrolysis was carried out in the same reaction vessel; thereby, reducing the isolation problem.

IV. EXPERIMENTAL

o-Bromobenzaldehyde Diacetate

This compound was prepared by the method of Tsang and Wood (43). In a three liter, three-necked, round bottom flask equipped with a mechanical stirrer and a thermometer, and surrounded by an ice bath, were placed one liter of glacial acetic acid, one liter of acetic anhydride, and 120 ml of concentrated sulfuric acid. When the solution was cooled to 0°C, 100 g (70 ml) of o-bromotoluene was added. After the solution reached a temperature of 5°, 170 g of chromium trioxide was added slowly at such a rate that the temperature did not rise above 10°C; about two hours were required for the addition. Stirring was continued for five hours after the chromium trioxide had been added. The reaction mixture was added to a crock that was one-half full of ice. The residue in the flask was washed out with ice water and the washings were added to the crock. When all the product had been transferred from the flask to the crock, the contents were stirred vigorously for 25-30 minutes. The reaction mixture was cooled in the refrigerator overnight. The product was filtered and washed with ice-cold water. The crude product was allowed to air dry and then recrystallized from ethanol. The yield of o-bromobenzaldehyde diacetate was 72-78 gm; (43-47%), M.P. 90-91°C.

o-Bromobenzaldehyde

28.7 g (0.10 mole) of o-bromobenzaldehyde diacetate was refluxed with 50 ml of concentrated hydrochloric acid and 150-200 ml water

for approximately one hour. The o-bromobenzaldehyde was steam distilled directly from the hydrolysis mixture. The distillate was separated from the water, dried and then placed in the refrigerator. The o-bromobenzaldehyde settled out as a solid. Yield, 22.2 g (78%). The o-bromobenzaldehyde was distilled under vacuum before being used. B.P. 118-119°C/12 mm.

o-Iodotoluene (44)

This compound was prepared by the method of Morgan and Coulson (45). A solution of 32.1 g (0.3 mole) o-toluidine in a solution of 60 g of concentrated sulfuric acid and 450 ml of water was diazotized at a temperature below 5° by the addition of a solution of 21 g of sodium nitrite in 60 ml of water. The resulting solution of the diazonium salt was filtered, and the filtrate was added to a solution of 60 g of potassium iodide in 60 ml of water. After standing one hour at room temperature, the mixture was warmed until evolution of nitrogen ceased. Sufficient solid sodium bisulfite was added to discharge the free iodine. The separated oil was removed by extraction with ether, and the ethereal solution was distilled after being washed with 10% aqueous sodium hydroxide and dried over calcium chloride. After removal of the ether by distillation, the residual oil was distilled from solid potassium hydroxide to give 35 g (54.0%) of the iodo-compound. B.P. 85-86°C/12 mm.

o-Iodobenzaldehyde (45,46)

This compound was prepared according to the method described in organic reactions, Vol. VIII, 210, 1954. A gently refluxing mixture of 87.2 g (0.4 mole) of o-iodotoluene, 240 ml of carbon tetrachloride, and 80 ml water containing a little iodine, irradiated by three 75-watt lamps, was treated during two hours with a solution of 48 g of bromine in 120 ml of carbon tetrachloride. After heating at reflux temperature for one additional hour, the solvents were removed as completely as possible by distilling from a steam bath. The organic layer was separated from the water, diluted with 60 ml of chloroform, and then heated in a boiling-water bath under reduced pressure until all the chloroform and water were removed. After cooling, a solution of 80 g of hexamine in 800 ml of chloroform was added to the residue and the mixture was allowed to stand overnight. The separated hexaminium salt was collected on a Buchner funnel, washed with a little chloroform, and dried in air for about one hour. The salt was then dissolved in a mixture of 120 ml of glacial acetic acid and 120 ml of water and heated at reflux temperature for one and one half hours. The mixture was cooled, diluted with water, and extracted several times with ether. The ethereal extracts were washed with sodium carbonate solution, then with water, and finally dried. Distillation under reduced pressure provided 25 g (27%) of a yellow oil which completely solidified to a light yellow solid, M.P. 30°C upon standing.

γ -o-Chlorophenylparaconic Acid

This compound was prepared by the method of Fuson (7). 12 g (0.12 mole) of succinic anhydride and 10 g (0.12 mole) of freshly fused sodium acetate were mixed in a mortar and the mixture dried at 100°C in the oven for half an hour. The mixture was placed in a flask, and 17.1 g (0.12 mole) of o-chlorobenzaldehyde was added at one time. The flask was fitted with an air condenser, and a calcium chloride drying tube. The flask was immersed in a wax bath at 140°C and kept at this temperature until the mixture began to turn dark and a moderate evolution of carbon dioxide was observed. The bath was allowed to cool to 120°C and was kept at this temperature for three hours. The crude product was steam distilled and 1.6 g of o-chlorobenzaldehyde was recovered. The liquid residue from the steam distillation was filtered while hot, to remove a tarry material. The filtrate was cooled in an ice bath and then acidified with concentrated hydrochloric acid. A white solid separated which was filtered with suction. A second crop of crystals was obtained by the evaporation of the mother liquid to one fourth of the original volume. The combined products were recrystallized from water-ethanol (10%) yield, 21.5 g (81.2%), M.P. 144-146°C. Infrared spectrum showed that the material gave absorptions consistent with the structure of γ -o-chlorophenylparaconic acid, and noted as follows: 3.30 - 3.81 μ , 5.66 μ , 5.78 μ , 6.81 μ , 8.43 μ , and 13.18 μ . Anal. Calculated for $C_{11}H_9O_4Cl$: C, 54.90; H, 3.77; Cl, 14.73. Found: C, 54.46; H, 3.77; Cl, 14.74.

γ -o-Bromophenylparaconic Acid

The γ -o-bromophenylparaconic acid was prepared from 12 g (0.12 mole) of succinic anhydride, 10 g (0.12 mole) of freshly fused sodium acetate and 21.4 g (0.11 mole) of o-bromobenzaldehyde. The procedure followed was identical with that used to prepare γ -o-chlorophenylparaconic acid. Yield, 24.6 g (75.3%). M.P. 155-156°C. It showed infrared adsorptions as follows: 3.30-4.00 μ , 5.71 μ , 5.81 μ , 6.81 μ , 8.50 μ , and 13.2 μ . Anal. Calculated for $C_{11}H_9O_4Br$: C, 46.34; H, 3.18; Br, 28.03. Found: C, 46.00; H, 3.25; Br, 28.49.

γ -o-Fluorophenylparaconic Acid

The γ -o-fluorophenylparaconic acid was prepared from 8.1 g (0.081 mole) of succinic anhydride, 7.0 g (0.085 mole) of freshly fused sodium acetate and 10 g (0.081 mole) of o-fluorobenzaldehyde. The method followed was essentially the same as that described for the preparation of γ -o-chlorophenylparaconic acid, with the following modification. When the reaction began as evidenced by the vigorous evolution of carbon dioxide, the reaction vessel was removed from the 140°C oil bath and when the temperature dropped to 120°C was reimmersed in the oil bath. The reaction mixture was heated at this temperature for three additional hours. Yield, 11.4 g (62.0%). M.P. 156-158°C. It showed infrared absorptions at: 3.11-3.85 μ , 5.71 μ , 5.81 μ , 6.81 μ , 8.41 μ , and 13.81 μ . Anal. Calculated for $C_{11}H_9O_4F$: C, 58.93; H, 4.05; F, 8.47. Found: C, 58.98; H, 4.09; F, 8.24.

γ -o-Iodophenylparaconic Acid

The procedure followed for the preparation of γ -o-iodophenylparaconic acid was essentially that used to prepare γ -o-chlorophenylparaconic acid, with the same modification as noted in the preparation of γ -o-fluorophenylparaconic acid. Also the heating period was for five hours. The quantities of materials used were 5.4 g (0.054 mole) of succinic anhydride, 4.9 g (0.059 mole) of freshly fused sodium acetate, and 12.5 g (0.054 mole) of o-iodobenzaldehyde. Yield, 13.05 g (74.4%). M.P. 150-151°C. It showed infrared absorptions at 3.16-3.71 μ , 5.61 μ , 5.79 μ , 8.52 μ , 10.00 μ , and 13.21 μ . Anal. Calculated for $C_{11}H_9O_4I$: C, 39.78; H, 2.73; I, 38.21. Found: C, 40.04; H, 2.77; I, 37.99.

γ -o-Nitrophenylparaconic Acid

The γ -o-nitrophenylparaconic acid was prepared from 10.0 g (0.1 mole) of succinic anhydride, 9.0 g (0.11 mole) of freshly fused sodium acetate and 16.6 g (0.1 mole) of γ -o-nitrophenylparaconic acid. The procedure followed was essentially that used to prepare γ -o-chlorophenylparaconic acid with the same modification as noted in the preparation of γ -o-fluorophenylparaconic acid. Yield, 10.6 g (38.3%). M.P. 163-165°C. It gave infrared absorptions at 3.21-3.92 μ , 5.62 μ , 5.88 μ , 6.6 μ , 7.49 μ , 9.92 μ , 12.76 μ and 13.31 μ . Anal. Calculated for $C_{11}H_9O_6N$: C, 52.60; H, 3.61; N, 5.58. Found: C, 52.41; H, 3.50; N, 5.67.

Determination of the molecular weight of γ -o-Halophenylparaconic Acid.

The γ -o-halophenylparaconic acid was dissolved in 2 ml of ethanol and 25 ml of deionized water, and titrated with sodium hydroxide solution, using phenolphthalein as the indicator. The results are shown in the following table.

TABLE IX
Determination of Molecular Weight

<u>Acid</u>	<u>Sample Weight</u>	<u>NaOH used (0.1126 N)</u>	<u>Equiv. Weight</u>	<u>Expected Mol. Wt.</u>	<u>Found Mol. Wt.</u>
-F	0.4761 g	37.68 ml	112.22	224	224
-Cl	0.3358 g	24.72 ml	120.63	240	241
-Br	0.4621 g	28.77 ml	142.61	285	286
-I	0.3645 g	19.39 ml	166.91	332	333
-NO ₂	0.3973 g	27.93 ml	126.31	251	252

Decarboxylation of γ -o-Chlorophenylparaconic Acid

A mixture of 1.0 g γ -o-chlorophenylparaconic acid and 5 mg of potassium hydrogen sulfate in a 10 ml flask was immersed in an oil bath (Dow Corning, 550 fluid) at 230°. A vigorous evolution of gas occurred which gradually subsided, and after a period of seventy minutes there was no further evidence of decarboxylation. Distillation at reduced pressure with a rapid increase in temperature from 230° to 305°C within ten minutes afforded a slightly yellow oil which solidified on standing. The crude material was dissolved in ether, and extracted repeatedly with saturated sodium bicarbonate solution until the sodium bicarbonate

solution gave no cloudiness upon acidification. The ether layer was then extracted with 5% potassium hydroxide. Treatment of the alkaline solution with concentrated hydrochloric acid gave the crude 5-chloro-1-naphthol in 8.1% yield.

After acidification of the sodium bicarbonate solution, the crude γ -o-chloro-phenylisocrotonic acid precipitated. The solid was filtered with suction, washed with ice-cold water, and dried in a vacuum dessicator over calcium chloride. Yield, 0.58 g (71%). Recrystallization from petroleum-ether (B.P. 60-90°C) gave white crystals with a M.P. 84.5-86.5°C. The compound showed infrared absorptions at: 3.03-3.67 μ , 5.92 μ , 6.34 μ , 8.29 μ , 10.44 μ , and 13.39 μ . Anal. Calculated for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61; Cl, 18.03. Found: C, 61.25; H, 4.62; Cl, 18.02.

Decarboxylation of γ -o-Bromophenylparaconic Acid

A mixture of 3 g γ -o-bromophenylparaconic acid and 15 mg of potassium hydrogen sulfate was heated in an oil bath at 225°C for one hour and fifty minutes. Distillation under vacuum (c.a. 5 mm) at 225°C afforded a light yellow oil which solidified on standing. The crude material was dissolved in ether and extracted repeatedly with saturated sodium bicarbonate solution until the sodium bicarbonate solution gave no cloudiness upon acidification.

Extraction of the ethereal solution with 5% potassium hydroxide, followed by acidification yielded no naphthol derivative.

Acidification of the sodium bicarbonate solution precipitated the γ -o-bromophenylisocrotonic acid. The solid product was collected

in a Buchner funnel, washed with ice-cold water and dried in a vacuum dessicator. Yield, 1.97 g (77.5%). Recrystallization from petroleum-ether (B.P. 60-90°C) gave white crystals with a M.P. 101-103°C. The compound showed infrared absorptions at: 3.34-3.88 μ , 5.90 μ , 6.12 μ , 8.31 μ , 10.36 μ , and 13.56 μ . Anal. Calculated for $C_{10}H_9O_2Br$: C, 49.82; H, 3.76; Br, 33.15. Found: C, 49.90; H, 3.77; Br, 33.16.

Decarboxylation of γ -o-Fluorophenylparaconic Acid

A mixture of 3 g γ -o-fluorophenylparaconic acid and 15 mg of potassium hydrogen sulfate was heated in an oil bath in a distillation flask at 230°C for sixty-eight minutes. The decarboxylation mixture was processed in a manner analogous to that described in the decarboxylation of γ -o-bromophenylparaconic acid. Yield, 1.85 g (77%). M.P. 62-63°C. It gave infrared absorptions at: 3.30-3.81 μ , 5.91 μ , 6.33 μ , 6.73 μ , 8.14 μ , 10.25 μ , and 13.43 μ . Anal. Calculated for $C_{10}H_9O_2F$: C, 66.66; H, 5.04; F, 10.54. Found: C, 66.43; H, 4.90; F, 10.39.

Decarboxylation of γ -o-Iodophenylparaconic Acid

A mixture of 2.1 g γ -o-iodophenylparaconic acid and 10 mg of potassium hydrogen sulfate was heated in an oil bath in a distillation flask at 225°+3°C for sixty-five minutes. The decarboxylation mixture was processed in a manner analogous to that described in the decarboxylation of -o-bromophenylparaconic acid. Yield, 1.36 g (74%). M.P. 120-122°C. It gave infrared absorptions at: 3.28-3.86 μ , 5.87 μ , 8.3 μ , 10.32 μ , and 13.52 μ . Anal. Calculated for $C_{10}H_9O_2I$: C, 41.69;

H, 3.15; I, 44.05. Found: C, 41.79; H, 3.37; I, 44.15.

Determination of molecular weight of γ -o-Halophenylisocrotonic Acid

The γ -o-halophenylisocrotonic acid was dissolved in 2 ml of ethanol and 25 ml of deionized water, and titrated with sodium hydroxide solution, using phenolphthalein as the indicator.

TABLE X
Determination of Molecular Weight

<u>Acid</u>	<u>Sample Weight</u>	<u>NaOH used (0.0981 N)</u>	<u>Expected Mol. Wt.</u>	<u>Found Mol. Wt.</u>
F	0.4431 g	24.99 ml	180	180
Cl	0.3925 g	20.37 ml	196	197
Br	0.3836 g	16.14 ml	241	242
I	0.3965 g	11.53 ml*	288	289
	0.6473 g	18.67 ml*	288	288

* 0.1201 N NaOH

Cyclization of γ -o-Chlorophenylisocrotonic Acid

In a 250 ml round bottom flask was placed 1.4 g of γ -o-chlorophenylisocrotonic acid, 0.60 g of anhydrous sodium acetate and 12.7 ml of acetic anhydride. The mixture was placed in an oil bath at 150°, irradiated with a U.V. light (Cenco Quartz Mercury arc U.V. region 2260 Å) and refluxed in an oil bath at 150°C for thirty-five minutes. After this period, 54 ml of 5% sodium hydroxide was introduced, and the mixture was refluxed for an additional fifteen minutes. Due to the fact that the mixture was still acidic (pH~6), 21 ml of 30% sodium

hydroxide was added. The mixture was refluxed for three hours during which time a red oil separated. After the mixture was filtered and the red oil was removed, the yellow solution was acidified with concentrated hydrochloric acid. Slightly yellow silky-like needles separated. Yield, 0.81 g (62.2%). The product was recrystallized once from hot water and then from petroleum-ether (B.P. 60-90°C). M.P. 131-132. It showed infrared absorptions at: 2.99-3.62 μ , 6.32 μ , 8.07 μ , 11.43 μ , and 12.92 μ . Anal. Calculated for $C_{10}H_7OCl$: C, 67.24; H, 3.95; Cl, 19.85. Found: C, 67.04; H, 4.02; Cl, 19.65.

Cyclization of γ -o-Bromophenylisocrotonic Acid

A mixture of 1.0 g of γ -o-bromophenylisocrotonic acid, 0.34 g of anhydrous sodium acetate and 7.3 ml of acetic anhydride in a 100 ml flask was refluxed in an oil bath at 150°C for thirty minutes. During this time the reaction mixture was irradiated with U.V. light. Hydrolysis was accomplished using 3.1 ml of 5% sodium hydroxide and 10 ml of 30% sodium hydroxide. The work-up and isolation were the same as that described for the cyclization of γ -o-chlorophenylisocrotonic acid. Yield, 0.4 g (51.1%). M.P. 135.5-136°C. It showed infrared absorptions at: 3.11-3.39 μ , 6.31 μ , 7.29-7.50 μ , 8.03 μ , and 12.97 μ . Anal. Calculated for $C_{10}H_7OBr$: C, 53.84; H, 3.16; Br, 35.82. Found: C, 53.61; H, 3.25; Br, 36.22.

Cyclization of γ -o-Fluorophenylisocrotonic Acid

A mixture of 2.43 g of γ -o-fluorophenylisocrotonic acid, 1.11 g anhydrous sodium acetate, and 23.6 ml of acetic anhydride in a 250 ml

flask was refluxed in an oil bath at 150°C for thirty minutes. During this time the reaction mixture was irradiated with U.V. light. 100 ml of 5% sodium hydroxide and 33 ml of 30% sodium hydroxide were used in the hydrolysis. The work-up and isolation were identical as that described for the cyclization of γ -o-chlorophenylisocrotonic acid. Yield, 0.81 g (46.5%). M.P. 129.5-130.5°C. It showed infrared absorptions at: 2.96-3.54 μ , 6.28 μ , 7.20 μ , 8.03 μ , 10.84 μ , and 12.94 μ . Anal. Calculated for $C_{10}H_7OF$: C, 74.07; H, 4.35; F, 11.72. Found: C, 73.80; H, 4.30; F, 11.69.

Cyclization of γ -o-Iodophenylisocrotonic Acid

A 100 ml flask containing 1.0 g of γ -o-iodophenylisocrotonic acid, 0.28 g anhydrous sodium acetate, and 6 ml acetic anhydride was refluxed in an oil bath at 150°C for thirty minutes. During this time the reaction mixture was irradiated with U.V. light. 26 ml of 5% sodium hydroxide and 8.5 ml of 30% sodium hydroxide were employed for the hydrolysis. The work-up and isolation were the same as that described for the cyclization of γ -o-chlorophenylisocrotonic acid. Yield, 0.38 g (40.5%). M.P. 126-127°C. It showed infrared absorptions at 2.98-3.34 μ , 6.28 μ , 8.04 μ , and 12.89 μ . Anal. Calculated for $C_{10}H_7OI$: C, 44.47; H, 2.61; I, 46.99. Found: C, 44.51; H, 2.80; I, 46.54.

V. SUMMARY

The γ -o-halophenylparaconic acids have been prepared in good yield by the application of the Perkin condensation using the o-substituted-benzaldehydes and succinic anhydride. The γ -o-nitrophenylparaconic acid was also prepared.

Attempted synthesis of γ -o-bromo and γ -o-chlorophenylisocrotonic acid under the same reaction conditions employed by Fittig and Jayne for the synthesis of γ ,phenylparaconic acid, resulted in a tarry material with no expected γ -o-halophenylisocrotonic acid.

Decarboxylation of γ -o-substituted-phenylparaconic acids was carried out at various temperatures, utilizing different solvents, and catalysts. Acid-catalyzed decarboxylation of γ -o-halophenylparaconic acid was found to be facilitated by potassium hydrogen sulfate. The time required for acid-catalyzed decarboxylation was reduced to one-half of that necessary for thermal decarboxylation. The yield of the γ -o-halophenylisocrotonic acids were: Cl, 71.0%; Br, 77.0%; I, 74.0%.

Infrared absorptions indicated that the γ -o-halophenylisocrotonic acid existed in the trans form.

The attempted cyclization of the trans γ -o-halophenylisocrotonic acid by refluxing with sodium acetate and acetic anhydride, gave negative results. Isomerization of the trans acid to the cis acid by ultra-violet irradiation, followed by refluxing with sodium acetate and acetic anhydride, afforded the cyclized product, 1-acetoxy-5-halonaphthol. The latter compound was easily hydrolyzed to the 5-halo-1-naphthol in good yield.

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