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Condensation reaction of terephthaladehyde and acetophenone

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University of the Pacific

CONDENSATION REACTION
OF TEREPHTHALADEHYDE AND ACETOPHENONE

A Thesis

Presented to

the Faculty of the Department of Chemistry

College of the Pacific

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Lloyd J. Mitchell

June 1955

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INTRODUCTION

The plant pigments constitute a fascinating group of compounds whose constitution has only recently been partially clarified. Roughly speaking, there are two main groups of pigments: the plastids, associated with the protoplasmic structure of plants, and the anthocyanins, generally found in solution in the cell sap. The term "anthocyanin" is derived from the Greek, "antho" signifying flower and "cyan" meaning blue, and was introduced by the botanist Marquart in 1835 to designate the blue pigments of flowers. It has since been extended to include all of the pigments of this group, the anthocyanin pigments being responsible for the innumerable shades of blue, red, violet, mauve, and magenta that are found in nature.

The anthocyanins are glycosides, the parent substance of the entire group being the heterocyclic nucleus benzo-pyrylium chloride (I) discovered by Decker and von Fellenberg (6)
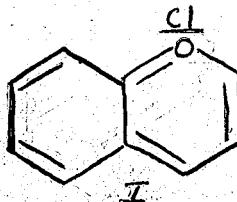
Substitution of a phenyl group in the 2- position yields 2-phenylbenzopyrylium chloride or flavylium chloride (II).

All members of this group to date may be regarded as poly-
hydroxy-2-phenylbenzopyrylium salts. 3, 5, 7- Trihydroxy-
flavylium chloride (III) is the simplest intact unit of
the anthocyanins.
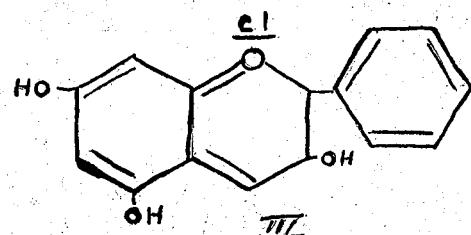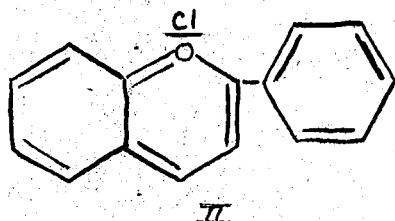
The sugar-free pigments, or aglucons, are called
anthocyanidins. The sugar residues are attached to the
3- or 3, 5- position, the 3, 5- diglucosides being the more
common.

The anthocyanidins are amphoteric, forming salts with
both acids and bases. As noted above, the salts with acids
are oxonuim salts. Use is made of this fact in the isola-
tion and purification of these pigments. The acid salts
are usually red, the metallic salts with bases blue, and
the neutral pigments purple.

The anthocyanidins are soluble in water and other com-
pounds having an hydroxyl group, but insoluble in benzene
and ether. They are isolated by dissolving the crude mat-
erial containing the pigments in alcohol containing hydro-
chloric acid and precipitated from the alcohol by the
addition of ether.

The flavones, a term derived from the Latin meaning

yellow, represent another very important group of pigments found in the plant kingdom. They occur very prevalently in combination with rhamnose or glucose as glycosides, and are frequently associated with the tannins. Their occurrence is readily demonstrated by placing a white flower in ammonia vapor. The deep yellow color which develops is typical of their reaction with alkalies.

The chemistry of the flavones bears a close similarity to that of the anthocyanidins. Our knowledge of these compounds is due largely to the work of von Kostanecki, Herzig, and A. G. Perkin from 1895 onward. The basic unit of the flavones is δ-pyrone. The relationship of δ-pyrone to flavone and flavenol is illustrated below:
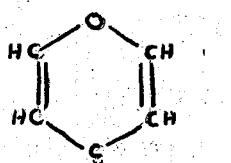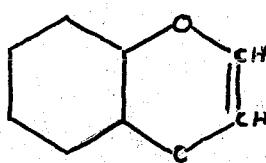
γ pyrone   benzopyrone
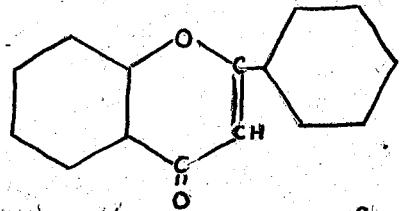
2-phenylbenzopyrone (flavone)   3-hydroxyflavone (flavenol).
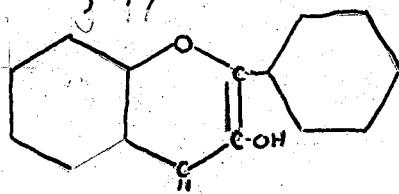
The flavones are yellow crystalline solids soluble in water, alcohol, mineral acids and alkalies. Their solubility in acids is due to the basic nature of the oxygen atom in the pyrone ring, which can become tetravalent with

formation of oxonium salts. These salts are highly colored
and are unstable in the presence of water, differing from
the anthocyanidins in this respect.

The key compound linking these two type compounds is
to be found in the substance benzalacetophenone, or chal-
cone. Chalcone is readily prepared by the condensation of
benzaldehyde and acetophenone in the presence of a dehydrat-
ing agent. Dry hydrogen chloride in ethyl acetate solution
was used in this work. The reaction for the preparation
of chalcone is given below:
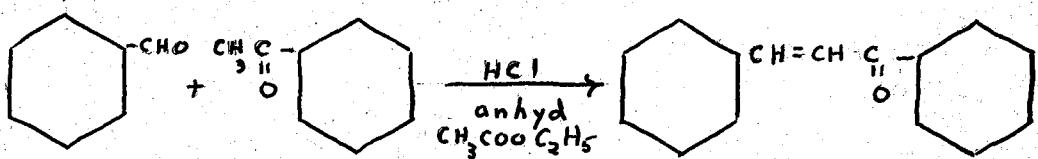
Using hydroxybenzaldehydes and hydroxy acetophenones many
derivatives of chalcone have been synthesized. Introduction
of hydroxy groups into the ring deepens the color.

Condensation of benzaldehyde and o-hydroxyacetophenone
yields 2-hydroxychalcone. Treatment of this compound with
hydrochloric acid gives a flavenone which, by bromination
followed by elimination of hydrogen bromide, produces
flavone.

The synthesis is outlined on the following page:
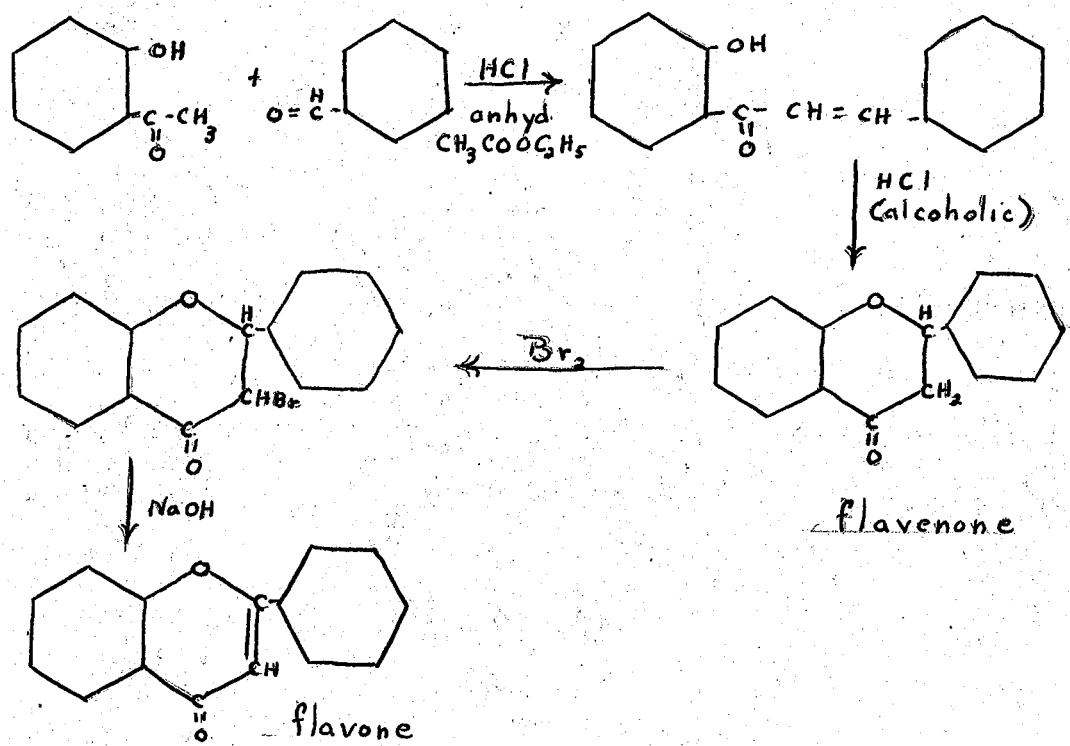
Treatment of flavenone with amyl nitrite and strong
hydrochloric acid in alcoholic solution yields an
isonitroso compound which forms flavenol on treat-
ment with dilute acid as outlined below:
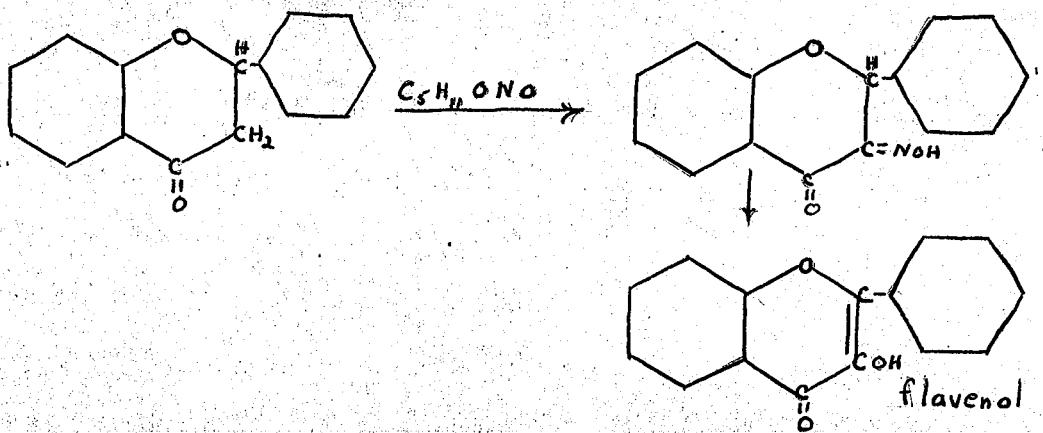
To form the anthocyanidins, the following synthesis
is applicable, proceeding via 2-hydroxy chalcone:

2-hydroxychalcone
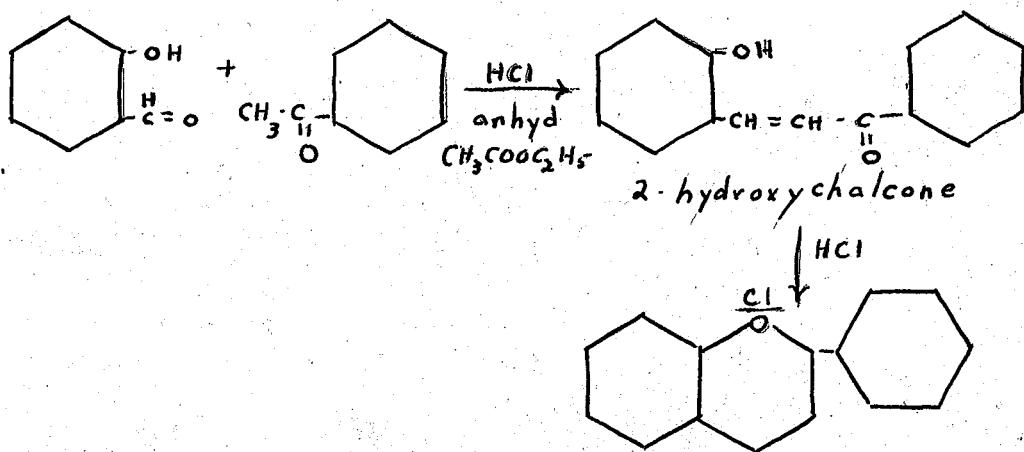
This method was employed extensively by Robinson (19, 20, 21) in the synthesis of the anthocyanidins. An alternate method, used by Willstatter in the synthesis of pelargonidin (IV) and cyanidin (V) involves the addition of an aryl Grignard to a coumarin.

IV

V
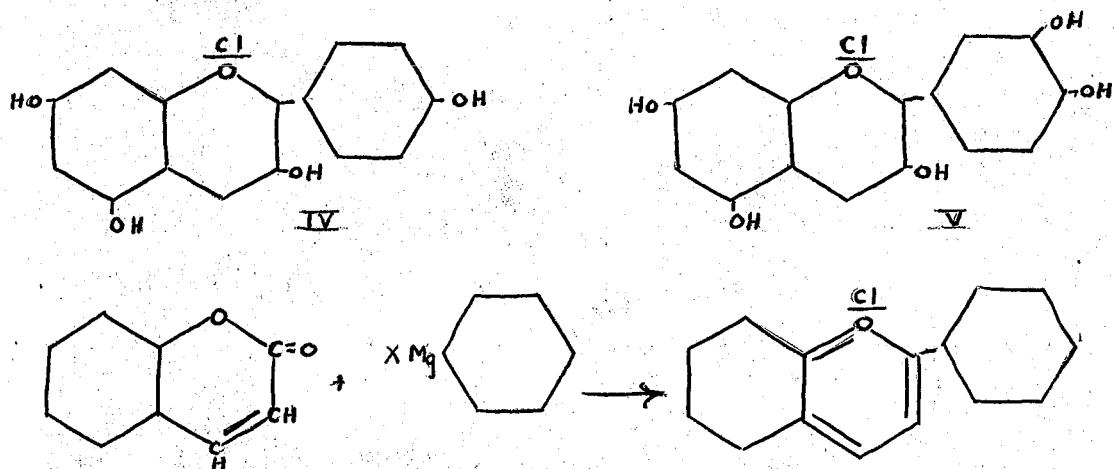
Chemical literature does not record work upon the condensation of dialdehydes with acetophenone and hydroxy derivatives of acetophenone and the dialdehyde. It is the purpose of this research to prepare one or more of the dialdehydes and investigate the nature of the condensation product with acetophenone.

The three isomeric dialdehydes, phthalaldehyde (IV),
isophthalaldehyde (VII) and terephthalaldehyde (VIII)

CHO
CHO   CHO   CHO
CHO   CHO

CHO
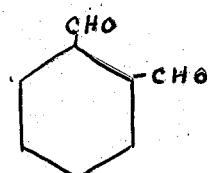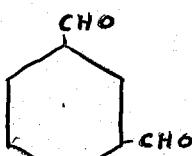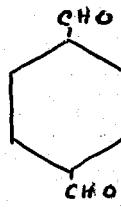
VI   VII   VIII

were prepared by Thiele, Gunther and Weitz (25, 26) by the
bromination of xylene in direct sunlight followed by hydro-
lsis with potassium oxalate solution.

CH₃   CHBr₂
CH₃   + Br₂ $\xrightarrow{\text{sunlight}}$ CHBr₂   + 4 HBr

CHBr₂   CHO
CHBr₂ + 2 $\begin{matrix}COOK\\COOK\end{matrix}$ + 2H₂O → CHO + 2 $\begin{matrix}COOH\\COOH\end{matrix}$
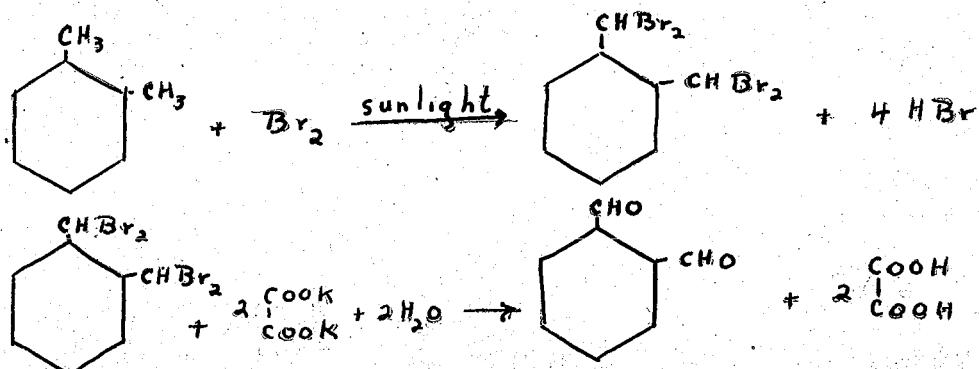
Various yields have been reported for the preparation
starting with o-xylene (8, 23, 25, 26). Due to the fact
that the best commercial grades of xylene are only about
90% pure, and also p-methylbenzyl bromide, an alternate
starting material, is a lachrymator, Wawzonek and Karll
(28) suggest the use of o-methyl benzyl chloride (pre-
pared according to the method of Smith and Spillane,
JACS 62, 2640 (1940). This was then brominated according
to the method of Snell and Weissberger (24). The over-all
process is outlined below:
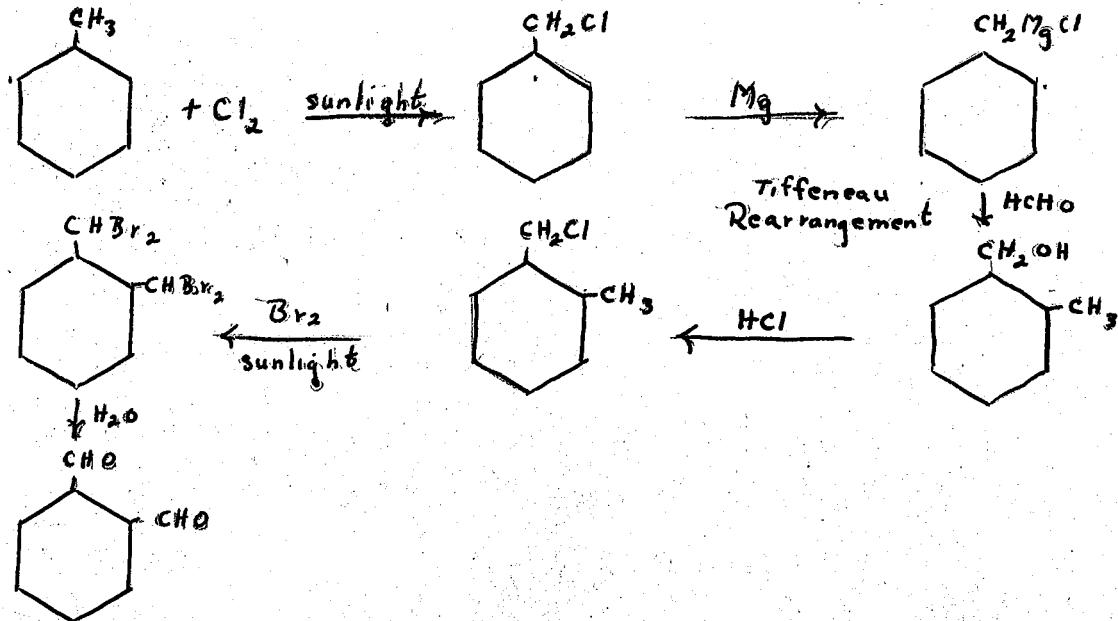
According to the method of Thiele and Gunther as described
in Shirley's Preparation of Organic Intermediates (38),
yields of 74 - 77 per cent of N,N,N',N'-tetrabrom-o-xylene
and 90 percent of phthalaldehyde are reported. Smith and
Spillane reported a 59 - 63 per cent yield of o-methylbenzyl
chloride. Wawzonek and Karll reported a 62 percent yield
of N,N,N',N'-tetrabrom-o-xylene based upon the o-methyl-
benzyl chloride.

Another approach to the problem involved the prepara-
tion of the acyl dichloride followed by reduction to the
dialdehyde. Ordinarily, however, the chlorides of dibasic
acids do not give good yields of dialdehydes. o-Phthalyl
chloride gives phthalide (22, 32). Dialdehydes are reported
from meta and paraphthalyl chloride in yields of about 80
percent. (9, 22).

Johnson and Williams (13) prepared iso-phthalaldehyde in 29-31 percent yield by the reaction of chromium trioxide and m-xylene in the presence of acetic anhydride. The reaction proceeds by way of the tetraacetate as indicated below:
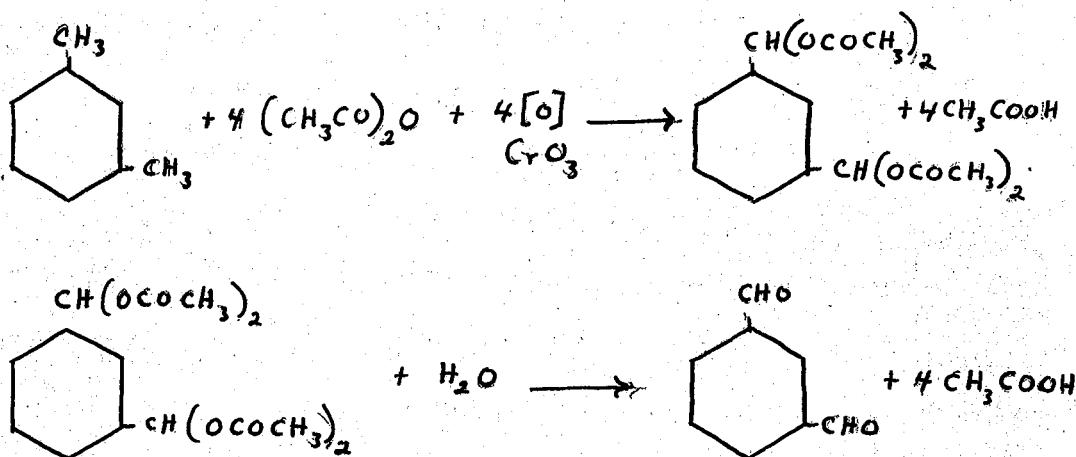
The Sommelet reaction is applicable to the preparation of meta and paradialdehydes, but not ortho, forming bis-(chloromethyl)benzenes. (31) Angyal and co-workers reported the preparation of terephthalaldehyde in 34 percent yield using 50 percent acetic acid. (2,3) The reaction involved combination of the bis-(chloromethyl)benzene with hexamethylenetetramine to form a salt which, upon heating with water yields the dialdehyde. Aqueous acetic acid (1:1) is recommended as solvent for the entire process, there being no need to insolate the intermediate. In some cases, however, the addition compound is first formed in chloroform, isolated, and then decomposed with water or dilute acetic acid.

Another method applicable to the preparation of tere-
phthalaldehyde involves the interaction of pyridinium
salts with p-nitroso demethylaniline. Substances contain-
ing reactive halogens, such as $ArCH=CHCH_2X$ or $ArCO_2CH_2X$,
as well as substituted benzyl halides $ArCH_2X$ readily
form pyridinium salts. Rearrangement of these products
with p-nitroso dimethylaniline to a nitrone followed by
acid hydrolysis yields the corresponding acid, B-unsat-
urated aldehyde, substituted glyoxal or aldehyde as the
case may be.

$$C_6H_4(CH_2Br)_2 + 2 \,\, \langle pyridine \rangle \longrightarrow C_6H_4\left[(CH_2\overset{+}{N}C_5H_5)\overset{-}{Br}\right]_2$$

$$\downarrow (CH_3)_2N-C_6H_4-NO$$

$$C_6H_4(CHO)_2 \underset{H_2O}{\overset{H^+}{\longleftarrow}} C_6H_4\left[CH=NO\,C_6H_4N(CH_3)_2\right]_2$$
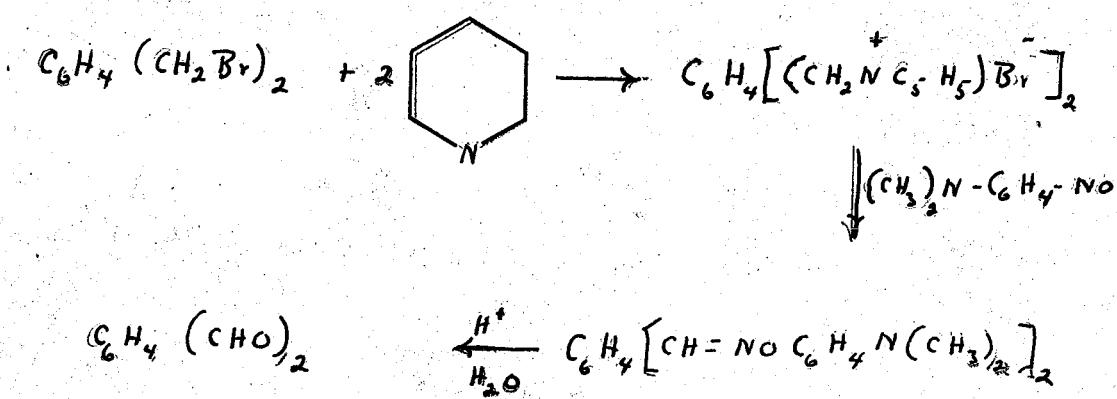
Tetephathalaldehyde has been prepared in this way in 70
percent yield (14, 15, 16, 18).

Weygand, Kinkel, and Tietjen (29) reported the pre-
paration of o-dialdehydes from o-dialcohols by way of
the cyclic selenous acid ester. The use of $LiAlH_4$ as a
reducing agent for dicarboxylic acids and their anhydrides
and esters makes the dialcohols readily available. The
latter are readily converted to the dialdehydes.
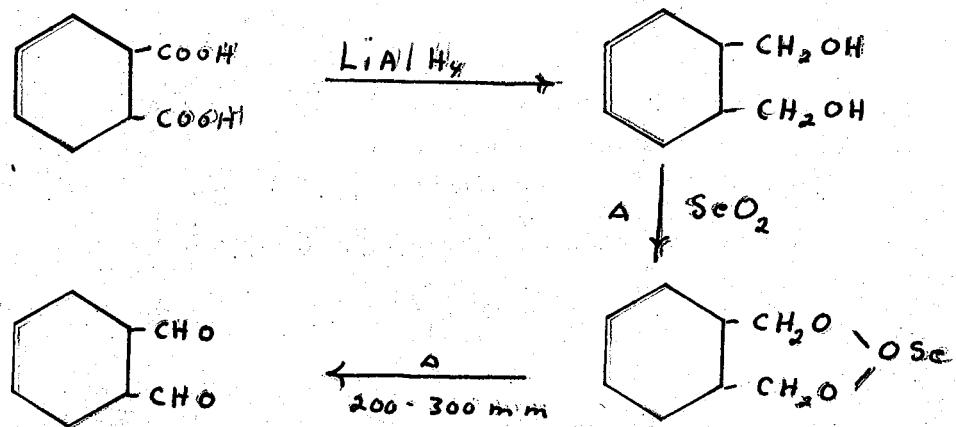
They report a 68 percent yield of phthalaldehyde by this
procedure.

Weygand and Tietjen (29) reported the preparation of
phthalaldehyde from N,N,N',N'-tetramethyl phthalamide by
treatment with LiAlH$_4$ in anhydrous tetrahydrofuran ether
medium.
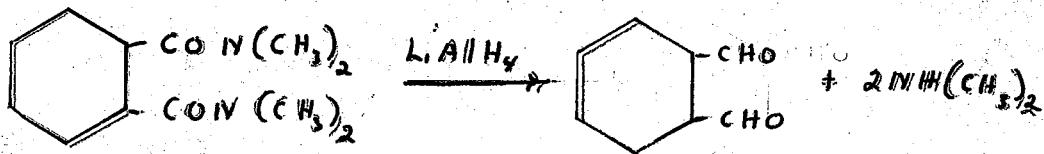
No yield was reported.

Hebbelynck and Martin (10, 11) used N-chlorocuccin-
imide in anhydrous solvents to oxidize primary and secondary
aryl alcohols to the corresponding aldehyde or ketone.

$$CH_3 / CH_3 + 2\ Cl_2 \longrightarrow CH_2Cl / CH_2Cl + 2\ HCl$$

$$\downarrow H_2O$$

$$CH_2OH / CH_2OH \xrightarrow[\text{reflux}]{CH_2-CO / CH_2-CO \searrow NH} CHO / CHO$$
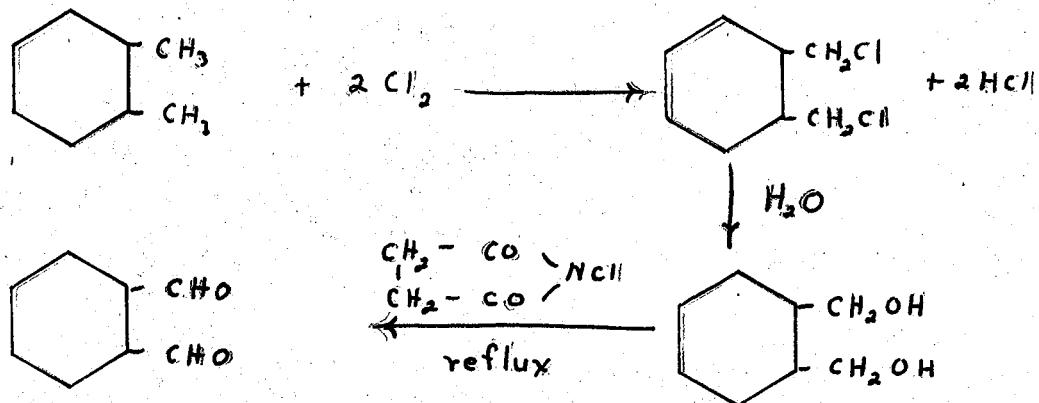
Yields of 12-77 percent are reported for this reaction. No yield was given for phthalaldehyde, but terephthalaldehyde was prepared in 22 percent yield.

Tomura (27), studying the pyrolysis and oxidation of alkylbenzenes, reported the presence of phthalaldehyde among the products formed by heating $o\text{-}C_6H_4(CH_3)_2$ at $350^\circ - 650^\circ$ with various amounts of oxygen.

Chaudhuri (4) reported a new synthesis of phthalalde-hyde and isophthalaldehyde involving the reaction of ben-zaldehyde and chloroform in the presence of aqueous potass-ium hydroxide followed by hydrolysis of the dichloro-meth-ylbenzaldehydes.

$$\text{—CHO} + CHCl_3 \xrightarrow{KOH} \text{CHO / CHCl}_2 \quad \text{and} \quad \text{CHO / CHCl}_2$$

$$\downarrow KOH,\ H_2O$$

$$\text{CHO / CHO} \quad \text{and} \quad \text{CHO / CHO}$$
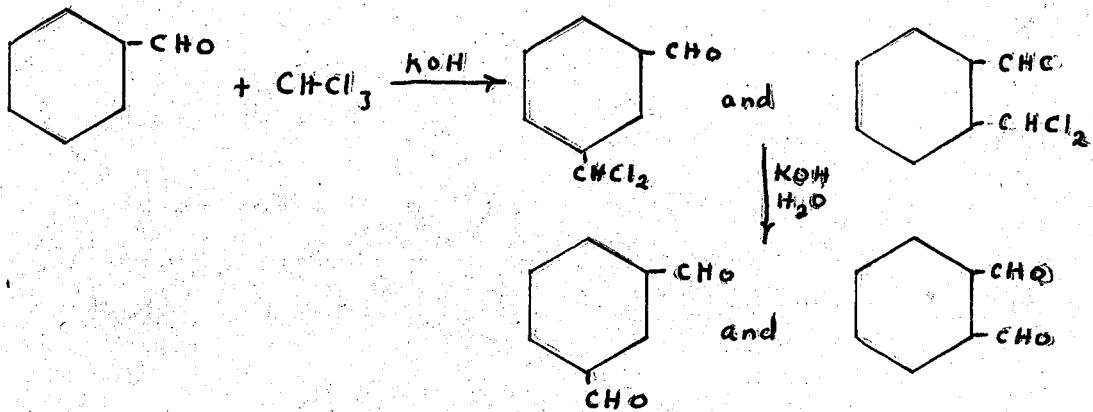
Several workers have failed to reproduce this reaction, however.

Two papers concerned with condensation products of isophthalaldehyde and terephthalaldehyde are of interest. Adams, Bullock and Wilson (1), in their study of the structure of benzidine, point out the extreme insolubility and high melting points of the condensation products of benzidine and isophthalaldehyde and terephthalaldehyde. Phillips (17), working on the preparation of synthetic curare substitutes, suggested the preparation of symmetrical "double-ended" molecules from terephthalaldehyde. The condensation of terephthalaldehyde and B-aminocrotonic ester is illustrated below:
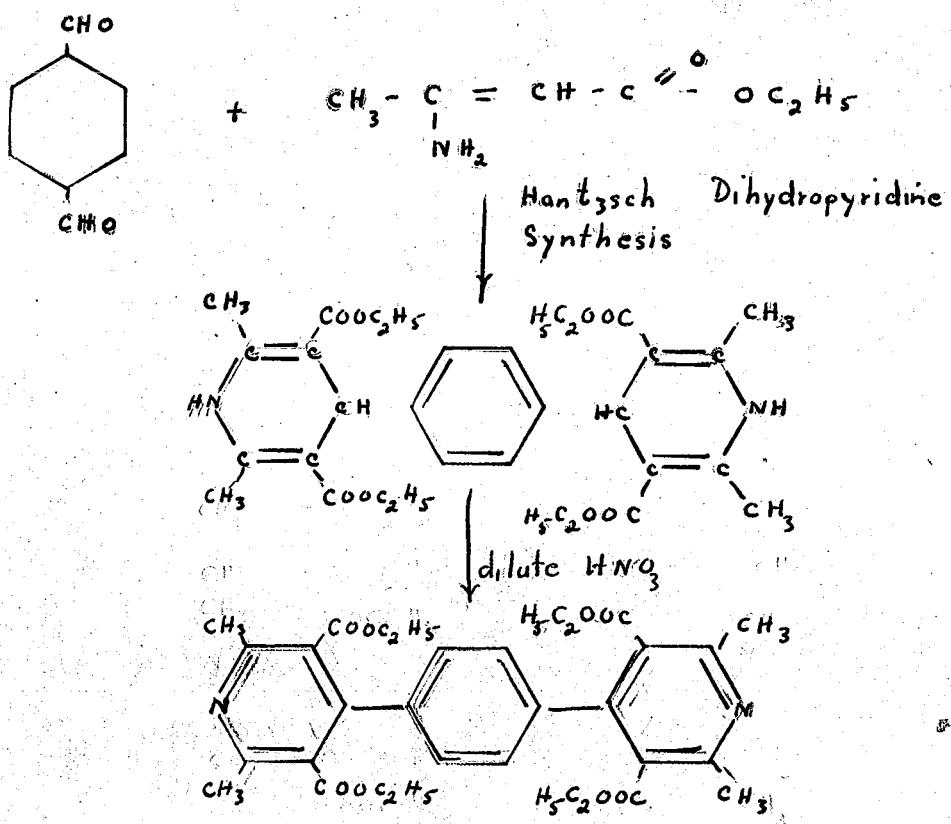
The dialdehyde was also reacted with 2- and 4- methyl
pyridine methiodides to give compounds of the type.

$$R - CH = CH - \langle\bigcirc\rangle - CH = CH - R$$
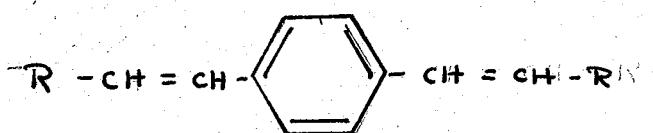
Experimental

Preparation of Intermediates:

Rectification of Xylenes:

The xylene used in the following preparations was derived from two sources: a mixture of the isomeric xylenes supplied by Central Valley Scientific Company and a sample of technical grade para-xylene supplied by Matheson, Bell and Coleman. An attempt was made to obtain a rough separation of the meta and para xylenes from the ortho isomer by distillation through a 120 inch column packed with glass helices and wrapped with sheets of abestos. The bulk of the material boiled between 137-140°C. Distillation of the combined bottoms from several runs yielded only a small fraction boiling 140-142°C. Lange gives the boiling point of o-xylene as 144°C.

Preparation of N,N,N',N'-Tetrabromo xylenes

Several brominations of xylene were carried out according to the general procedure of Thiele and Gunther (25) as described for o-xylene in Shirley's Preparation of Organic Intermediates (38) with the variations noted following in Table I. One mole (106g) of the xylene was placed in a one liter three-neck round bottom flask equipped with an efficient reflux condenser, a thermometer, and a dropping funnel. Cork stoppers wrapped with tinfoil were used. The reaction flask was set up outside in direct

sunlight and 642g. (200ml, 3.9 mols) of dry bromine were added slowly over 3-4 hours. The rate of addition of the first 125-150 ml. of bromine was governed by the rate at which the bromine color was discharged. Following the addition of the bromine the reaction mixture was heated slowly to 150-160°C, and maintained at this temperature for at least two hours. Upon cooling the solid was washed with a small amount of chloroform and recrystallized from this solvent.

Although Thiele and Gunther reported a 74-77 percent yield of N,N,N',N'-tetrabromo-o-xylene, the writer was unable to obtain comparable yields with the mixtures of meta and para-xylenes used. The reaction mixtures in every case showed evidence of considerable charring and decomposition, and a relatively large proportion of each run consisted of a thick, viscous oil which defied further attempts at purification. Considerable amounts of the N,N'-dibromo xylenes were obtained. As noted in Table I, runs 2 and 6 were the only ones in which any of the N, N,N',N'-tetrabromo-p-xylene was recovered, and in each of these a longer heating period at 150-160°C was employed.

TABLE I

Bromination of Xylene Fractions

Run No.	Fraction Brominated	Conditions	Products *
1	137-138°	Poor illumination Product distilled	163 g. bp 155°/6mm yielded crystals on standing of N,N,N'N'-tetrabromo-m-xylene mp 107°C
2	137-138°	Kept at 150-160° for three hours	25g (o.o6 mol) N,N,N',N'-tetrabromo-p-xylene mp 169°
3	p-xylene (commercial)	heavy precipitate after addition about 70 ml Br$_2$	79.5g (o.30 mol) N,N'-dibromo-p-xylene
4	p-xylene (commercial)	Reaction mixture heated during Br$_2$ addition	28.5g (o.11 mol) N,N'-dibromo-p-xylene
5	140-142°	Product distilled	210.5g (o.80 mol) N,N'-dibromo-p-xylene
6	137-138°	Kept at 150-160° for five hours	32.5g (0.08 mol) N,N,N'N'-tetrabromo-p-xylene

*No material balance was obtained in these runs. Only the product isolated is listed, the rest of the material appearing as bottoms. The N,N'-dibromo xylenes obtained in most of the runs listed above is a powerful lachyrmator, and hence is very unpleasant to work with. Owing to the

difficulties encountered in the purification of the rather
complex reaction mixtures obtained in the brominations, it
was deemed advisable to hydrolyze the relatively pure frac-
tions isolated to the corresponding dialdehydes whose
separation is considerably simpler.

Terephthalaldehyde via N, N, N', N'-Tetrabromo-p-Xylene:

The N,N,N',N'-tetrabromo-p-xylene, m.p. 169°C, was
converted to terephthalaldehyde by the method of Thiele
and Gunther (25) as described in Shirley's Preparation of
Organic Intermediates (38). A mixture of 25g (0.06 mol)
N,N,N',N'-tetrabromo-p-xylene, 22.5g (0.14 mol) potassium
oxalate, 156 ml. of distilled water and 156 ml. 95 percent
ethanol was refluxed for forty hours. Then the condenser
was set downward for distillation, and 140-150 ml. of ethyl
alcohol removed by distillation. Redistillation of the
alcohol yields a small portion of terephthalaldehyde.

Sodium phosphate (44g) was added to the reaction
mixture and the mixture was steam distilled. The ethanol
coming over first was collected separately and added to
another batch. The terephthalaldehyde steam distilled
slowly, tending to separate in the condenser from which
it was easily removed with a little boiling water. Re-
crystallization from water yielded long white needles;
m.p. 116°C, (Lit. 116°C) in about 70 percent yield.

Terephthalaldehyde via CrO₃ Oxidation of p-xylene:

In a one liter, three-neck flask, equipped with a

mechanical stirrer, a dropping funnel, and a thermometer, were placed 12.5g. (0.16 mol) p-xylene, 500g. (464 ml., 4.9 mols) of acetic anhydride, and 200g (191 ml., 3.3 mols) glacial acetic acid. The reaction mixture was stirred and kept at 5-10°C while 75g. (41.5 ml., 0.77 mol) concentrated sulfuric acid was added slowly. Then, over a period of about 1½ hours, 45g (0.45 mol) of chromium trioxide was added in small amounts taking care that the temperature did not rise above 10°C. After the addition was complete, stirring was continued for two hours.

Next the reaction mixture was poured rapidly into one liter of cracked ice, with vigorous stirring, and extracted with three 125 ml. portions of chloroform. These extracts were kept separate and used to wash the decomposition mixture from a second experiment run in the same manner. The extracts were then combined, washed with water, and dried over anhydrous magnesium sulfate.

The drying agent was removed by filtration and the bulk of the chloroform removed by distillation. Upon cooling 8g of the tetraacetate separated. This material, after two washings with boiling water, and drying, melted at 160-165°C.

The solid was suspended in a solution of 100 ml. of water and 10 ml. of 85 percent phosphoric acid, and steam distilled. After removal of 10-15 ml of chloroform, the terephthalaldehyde distilled slowly, solidifying in the

condenser. A yield of 2 g. (6 percent), m.p. 116°C was obtained.

Terephthalaldehyde via Sommelet Reaction

A solution of 30.5 g. (0.12 mol) of N,N'-dibromo-p-xylene in 300 ml. of chloroform and a solution of 32 g. (0.23 mol) of hexamethylene tetramine in 300 ml. of chloroform were prepared separately. Upon mixing a flocculent brown precipitate formed within 10-15 minutes. The resultant mixture was heated under reflux for two hours to insure complete precipitation of the salt. The chloroform was removed by distillation and 500 ml. of water added to the residue. This residue was refluxed for 3-4 hours, during which time an oil gradually formed. Upon cooling, 44 g. of sodium phosphate were added and the mixture steam-distilled. The first portion of distillate was cloudy and the odor of dimethylamine was evident. Continued heating with the addition of 60 ml H_2O and 40 ml 85 percent phosphoric acid yielded 4 g. terephthalaldehyde. (25 percent yield)

Acetophenone

Eastman Kodak grade acetophenone was used without further treatment in the condensation.

Phenyl Acetate

A solution of 282 g. (3.0 mols) of phenol and 306 g. (3.0 mols) of acetic anhydride was refluxed for 14 hours and then distilled under reduced pressure to yield 361 g.

of phenyl acetate b.p. 95-96°/25 mm. (88.5 percent).

o-Hydroxy acetphenone

o-Hydroxy acetophenone was prepared from phenyl acetate by the Fries reaggangement. In a one liter, three-neck flask provided with a reflux condenser, thermometer, and mechanical stirrer were placed 136 g. (1.0 mol) of phenyl acetate. Then 173 g. (1.3 mols) of anhydrous aluminum chloride were added slowly, maintaining the temperature between 20-80°C. The mixture became very thick, making stirring difficult. Following the addition of the aluminum chloride, the reaction mixture was heated in an oil bath to 120-130°C for 20 minutes. Upon cooling it set to a firm resin.

The resinous material was decomposed by the addition of dilute sulfuric acid and extracted with diethyl ether. The ether was removed by distillation and the residue distilled under reduced pressure. A fraction boiling at 109-133°C/24 mm was collected and redistilled to yield 26g. of o-hydroxy acetophenone b.p. 110-113°/22-23 mm. (19 percent yield).

A higher boiling fraction of the first distillation (68g., b.p. 167-168/6 mm), upon recrystallization from benzene with charcoaling yielded 24g of p-hydroxyacetophenone, m.p. 109°C (18 percent yield)

Preparation of Chalcones

Condensation of Terephthalaldehyde and Acetophenone

Dry hydrogen chloride was bubbled through a solution

of 5g. (0.04 mol) terephthalaldehyde and 9g. (0.08 mol) acetophenone in 250 ml. of dry ethyl acetate maintained at ice temperature for 12 3/4 hours. This treatment was carried out over a period of two days, the solution being placed in a refrigerator overnight. The solution first turned yellow and gradually darkened to a deep red color. A salmon-colored precipitate separated on standing overnight.

The condensation product showed little tendency to dissolve in any of the common solvents. It was insoluble in 50 percent, 80 percent, and 95 percent ethanol, water, diethyl ether, benzene, chloroform, dioxane, acetone, ethyl acetate and glacial acetic acid. It dissolved to a limited extent in warm cyclohexanone.

The material was purified by extracting once with boiling water and twice with hot 95 percent ethanol and dried in a desiccator over concentrated sulfuric acid. It was a pale salmon-colored solid, m.p. 195-196°C. It did not reduce Fehling's solution and gave a negative test with Tollen's reagent. Its molecular weight, determined cryoscopically in camphor in which it is soluble, was 334 (calcualted for $C_{24}H_{18}O_2$ - 338). The yield was nearly 100 percent.

Analysis:

Calculated for $C_{24}H_{18}O_2$: C 85.2; H 5.4; O 9.5

Found: C 84.9; H 5.2; O 9.9

The absorption spectrum of the compound was determined in cylclohexanone solution using a Beckman Model B spectrophotometer.

Condensation of Terephthalaldehyde and o-Hydroxy aceto Phenone.

An unsuccessful attempt was made to condense terephthalaldehyde and o-hydroxy acetophenone using the same procedure as described above for acetophenone. A subject for further investigation might be the benzoylation of o-hydroxy acetophenone and condensation of the resulting o-benzoylacetophenone with terephthalaldehyde. Following condensation the benzoyl group will be removed by hydrolysis and the hydroxy terephthalcone recovered.

Absorbance

Wave Length, mμ

0.5 Percent Solution of
Terephthalal - diacetophenone
in Cyclohexanone
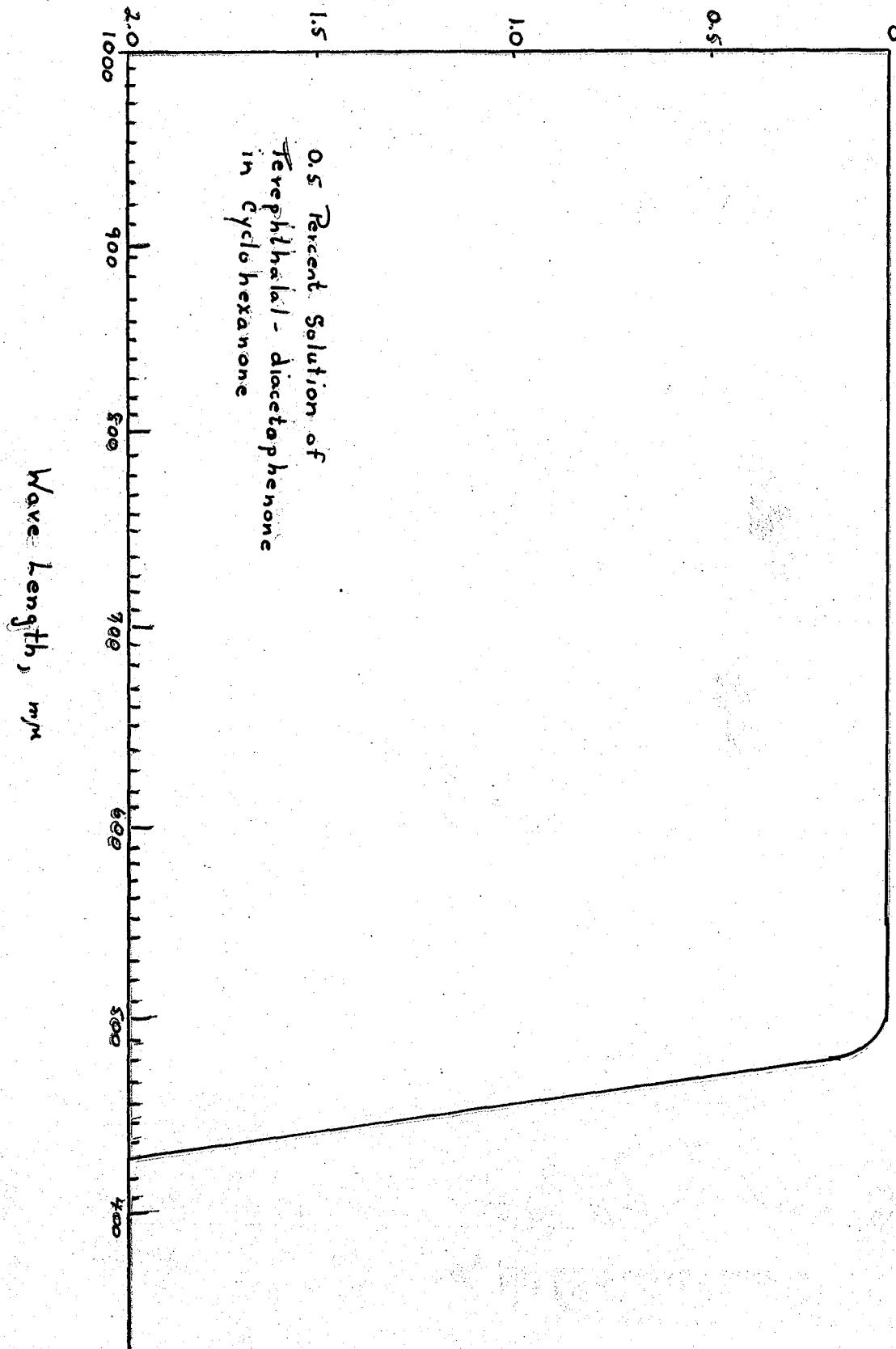
Summary

The preparation of dialdehydes, with particular em-
phasis upon terephthalaldehyde, has been investigated. The
three methods considered were: (1) The method of Thiele
and Gunther involving bromination of xylene followed by
hydrolysis of the tetrebromo-xylene, (2) the chromic acid
oxidation of xylene in acetic anhydride-acetic acid media
followed by hydrolysis of the tetraacetate and (3) the
Sommelet reaction involving bromination of xylene to form
the bis-(bromomethyl) xylene, reaction with hexamethy-
lenetetramine and hydrolysis of the resultant salt.

In spite of several inherent disadvantages, the method
of Thiele and Gunther proved to be the most feasible. The
disadvantages of this method are: (1) The difficulty of
obtaining pure ortho, meta, or para xylene to start with,
(2) the difficulty of separating the complex mixture of
products obtained upon the bromination of commercial
xylene, (3) the low yield of the desired N,N,N',N'-tetra-
bromo-p-xylene and (4) the formation of relatively large
amounts of the N,N'-dibromo-xylenes which are powerful
lachrymators. However, the N,N'-dibromo-xylenes can be
converted to the corresponding dialdehyde by means of the
Sommelet reaction, thus compensating to some extent for
the low yield of N,N,N',N'-tetrabromo-p-xylene obtained.

Terephthalaldehyde was condensed with acetophenone in
dry ethyl acetate solution using dry hydrogen chloride as

the condensing agent. Nearly a 100 percent yield of
product was obtained. This material melted sharply at
195-196°C and was characterized by a lack of solubility
in any of the common organic solvents. It was identified
by analysis and molecular weight determination as tere-
phthalal-diacetophenone
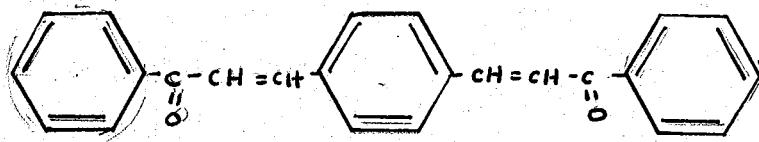
The compound has not been prepared before. It is the
parent of a new series of compounds that may be prepared
from the hydroxylated acetophenones and phthalaldehydes.
The name phthalcone is assigned to the parent compound.

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