Summary

1. The condensation reaction between carbon tetrachloride and phenol has been investigated in detail. Eight of the nine products formed have been identified, and this made it possible to give an interpretation as to the mechanism of the condensation reaction.

2. Aurin is the chief product formed. Methods have been worked out for obtaining it quite pure, and a number of new derivatives of aurin have been prepared.

3. In addition to aurin, the following substances were isolated from the condensation mixture: leuco-aurin, *o,p',p''*-trihydroxytriphenyl carbinol, *p*-hydroxyphenyl-fluorone, *p*-hydroxyphenyl-xanthane, diphenyl carbonate, di-*p*-hydroxybenzophenone and *o,p'*-dihydroxybenzophenone.

4. It is possible to alter the conditions in the process of the condensation reaction in such a manner that, instead of aurin, diphenyl carbonate or di-*p*-hydroxybenzophenone becomes the chief product of the reaction. This procedure furnishes excellent preparative methods for these two substances. The decomposition of *p*-hydroxyphenyl-fluorone by alkali and air furnishes a very good method of preparing *o,p'*-dihydroxybenzophenone.

5. Aurin and its derivatives, such as the triacetyl and tribenzoyl carbinol, possess in a notable degree "residual affinity," and they give rise to many loosely bound combinations with alcohol, ether, ketones, carbon tetrachloride, aromatic hydrocarbons, etc.

6. It was found that the method hitherto employed for making aurin—namely, from phenol and oxalic acid—gives less by-products than the carbon tetrachloride method, but furnishes no better yields and is wasteful because it requires the use of a large excess of oxalic acid.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO]

SOME DERIVATIVES OF ACENAPHTHENE

BY FRED. R. LORRIMAN

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Acenaphthene on oxidation gives naphthalic acid, and naphthalic anhydride has been described as resembling phthalic anhydride. It seemed to be worth while to determine whether naphthalic anhydride could be substituted for phthalic anhydride in the reaction with benzene and aluminum chloride.

The acenaphthene was oxidized by sodium dichromate in glacial acetic acid as described by Graebe and Gfeller[1] and converted into the anhydride by sublimation. This naphthalic anhydride was used with benzene and

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[1] Graebe and Gfeller, *Ber.*, **25**, 652 (1892).

aluminum chloride, but although the experiment was tried under various conditions the only acid recovered from the product was naphthalic acid. The experiment was repeated using 4-bromonaphthalic anhydride prepared from 4-bromo-acenaphthene but this was also unsuccessful. It was also unsuccessful when naphthalic anhydride was used with toluene or with naphthalene either alone or in benzene solution.

Graebe,[2] using phthalic anhydride, aluminum chloride and acenaphthene in carbon disulfide solution, obtained a 75% yield of 4-acenaphthoyl-benzoic acid (1,2). The writer, using phthalic anhydride, freshly distilled aluminum chloride, and acenaphthene in benzene solution, at room temperature, obtained a 90% yield and obtained no *o*-benzoyl-benzoic acid. This corresponds with the finding of McMullen[3] that naphthalene or anthracene might be used in benzene solution and no benzoyl-benzoic acid obtained.

The 4-acenaphthoyl-benzoic acid was fused with potassium hydroxide at 225° for ten minutes and although the greater part of the product was phthalic acid and acenaphthene, some benzoic acid and 4-acenaphthoic acid were obtained. This agrees with the finding of Graebe that the acid is 4-acenaphthoyl-benzoic acid (1,2). The methyl ester, m. p. 73–74°, and the ethyl ester, m. p. 84–85°, of the 4-acenaphthoic acid were prepared.

Action of Acetic Anhydride on 4-Acenaphthoyl-benzoic Acid (1,2).—Two g. of the acid was warmed on the water-bath for two minutes with 40 cc. of acetic anhydride in which it dissolved. As the solution cooled, amber colored, hexagonal plates separated which melted at 131–132° and appeared to decompose at 165° giving a product that did not melt at 300°. This latter product is obtained directly when the acid is heated at 100° for ten hours with acetic anhydride. The acetyl derivative, m. p. 131–132°, is insoluble in ether and soluble in acetone and benzene; with potassium hydroxide it gives potassium acetate and the potassium salt of 4-acenaphthoyl-benzoic acid.

Preparation of Phenyl-4-acenaphthylphthalide. The Rubidge and Qua Reaction.[4]—Ten g. of freshly distilled phthalic anhydride in 100 cc. of benzene was treated with 18 g. of aluminum chloride. After being kept cool for two hours it was heated on the water-bath for three hours and then 12 g. of acenaphthene dissolved in 50 cc. of benzene and 7.5 cc. of acetic anhydride was added and the mixture was again heated on the water-bath for 20 hours. About 2 g. of *o*-benzoyl-benzoic acid was obtained. The residue insoluble in dil. sodium hydroxide was dried at 50° and triturated several times with acetone which removed the gummy material leaving the phthalide; yield, 13 g. The phthalide, m. p. 216–217°, is soluble in chloro-

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[2] Graebe, *Ann.*, **327**, 100 (1903).

[3] McMullen, This Journal, **44**, 2055 (1922).

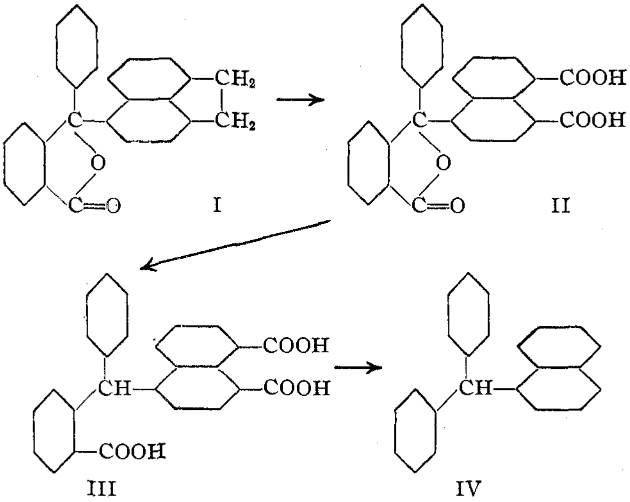
[4] Rubidge and Qua, *ibid.*, **36**, 732 (1914).

form, ether, hot benzene and hot acetic acid and sparingly soluble in hot ethyl alcohol. It is soluble in concd. alkali solution but is precipitated again on dilution.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 85.86; H, 5.01. Found: C, 85.8; H, 5.27.

Preparation of Tolyl-4-acenaphthylphthalide.—This phthalide was prepared in the same way as the phenyl-4-acenaphthylphthalide using toluene instead of benzene. No *p*-toluyl-benzoic acid was obtained. The phthalide was quite soluble in dil. alkalies, but because of its colloidal condition it was very difficult to purify and no satisfactory melting point or analysis was obtained. As toluene always reacts in the *para* position in Friedel and Crafts' reaction it is reasonable to assume that this is *p*-tolyl-4-acenaphthylphthalide.

Identification of Phenyl-4-acenaphthylphthalide.—The phthalide (I) was oxidized giving Compound II which on reduction gave Compound III. The barium salt of III on distillation gave α-naphthyl-diphenyl-methane (IV).



Details of these preparations are given in Table I, as are the details of other preparations from 4-acenaphthoyl-benzoic acid and from the phthalides. The 4-acenaphthyl-phenyl-methane, m. p. 111–112°, may be compared with Dziewonski's[5] 3-acenaphthyl-phenyl-methane, m. p. 112°. Also the oxime of 4-benzoyl-naphthalic acid, m. p. 244 with decomposition, and the imide, m. p. 252°, were prepared and have the same melting points as the oxime and imide of 3-benzoyl-naphthalic acid prepared by Dziewonski. In spite of these similarities the preparation of α-benzyl-naphthalene from the benzoyl-naphthalic acid leaves no doubt that it and the other compounds prepared from it are 4-derivatives.

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[5] Dziewonski, *Bull. soc. chim.* [III] **31,** 373, 923 (1904).

TABLE I

DERIVATIVES OF ACENAPHTHENE

Compd. No.	Name	Formula[a]	Source[a]	Method[b]	M. p.	Solubility, etc.
1	4,5 - Dicarboxy - 1-naphthyl - phenylphthalide	II	I	1	291° (anhydride)	Cryst. from acetic acid
2	4,5 - Dicarboxy - 1-naphthyl - *o* - carboxy - phenyl - methane	III	II	4	206° (anhydride)	Cryst. from acetic acid
3	α - Naphthyl - diphenylmethane	IV	III (Ba salt)	5		Refs. 7, 8
4	*o* - Carboxy - phenylphenyl - 4 - acenaphthylmethane	$HO_2C.C_6H_4.CH=(C_6H_5)(C_{12}H_9)$	I	2	220° (methyl ester 135–136°)	Very soluble in chloroform, acetone and hot benzene
5	4 - Acenaphthyl - diphenylmethane	$C_{12}H_9.CH=(C_6H_5)_2$	Ba salt of (4)	4 (washed with hot methyl alcohol)	176° (from ether)	Very soluble in benzene and toluene; no compound with picric acid
6	4,5 - Dicarboxy - 1-naphthyl - diphenylcarbinol	$(C_6H_5)_2=C(OH)—C_{10}H_5(CO_2H)_2$	(5)	1	209° (anhydride)	Soluble in ether and acetic acid. Benzophenone and naphthalic acid were also obtained
7	4,5 - Dicarboxy - 1-naphthyl - *p* - carboxy-phenylphthalide		Tolyl analog of I	1	245° (anhydride)	Sol. in benzene, chloroform, acetone, methyl alcohol
8	*o* - Carboxy - phenyl - *p*-tolyl - 4 - acenaphthylmethane	$HO_2C.C_6H_4.CH=(C_7H_7)(C_{12}H_9)$	Tolyl analog of I	2	210° (from alcohol) methyl ester 147°	
9	Phenyl - *p* - tolyl - 4-acenaphthylmethane	$(C_6H_5CH(C_7H_7)C_{12}H_9)$	(8)	5 (washed with hot alcohol)	209°	Sol. in ether and hot acetic acid

TABLE I (*Concluded*)

DERIVATIVES OF ACENAPHTHENE

Compd. No.	Name	Formula[a]	Source[a]	Method[b]	M. p.	Solubility, etc.
10	4 - Acenaphthylphthalide		4-acenaphthoylbenzoic acid (1,2)	3	206° (from chloroform)	
11	*o* - Carboxy - phenyl - 4-acenaphthylmethane	$HO_2C.C_6H_5CH_2C_{12}H_9$	4-acenaphthoylbenzoic acid (1,2)	4	215–216°	Sol. in chloroform, hot benzene, hot acetic acid
12	4 - Acenaphthyl-phenylmethane	$C_6H_5.CH_2.C_{12}H_9$	Ba salt of (11)	5 (40–50 mm.)	111–112°	Very sol. in benzene; sol. in hot acetic acid
13	4 - Benzoyl - naphthalic acid	$C_6H_5.CO.C_{10}H_5(CO_2H)_2$	(12)	1	194° (anhydride)	Described by Graebe
14	4 - Benzylnaphthalic acid	$C_6H_5.CH_2.C_{10}H_5(CO_2H)_2$	(13)	2	162° (from hot alcohol) anhydride, 170°	
15	(α) - 4-Benzyl-naphthalene		Ba salt of (14)	5 (40–50 mm.)	59°	Ref. 9
16	*o* - Carboxy - benzoyl-naphthalic acid (1,4)	$HO_2C.C_6H_4.CO.C_{10}H_5$-$(CO_2H)_2$	4-acenaphthoylbenzoic acid (1,2)	1	234° (anhydride)	Ref. 10
17	*o* - Carboxy - benzyl-naphthalic acid (1,4)	$HO_2C.C_6H_4.CH_2C_{10}H_5$ $(CO_2H)_2$	(16)	4	266°	Sol. in hot acetic acid; slightly sol. in hot acetone; insol. in benzene and alcohol
18	(?) - Benzyl - naphthalene		Ba salt of (17)			

[a] Roman numerals indicate structural formulas in the text.

[b] The methods used were the following: (1) Oxidation with dichromate in acetic acid; (2) reduction by zinc in alcoholic potassium hydroxide solution; (3) reduction by zinc in ammoniacal solution; (4) reduction by the method of Scholl and Neovius;[6] (5) distillation with an excess of barium hydroxide.

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[6] Scholl and Neovius, *Ber.*, **44**, 1080 (1911).

[7] Acree, *Ber.*, **37**, 617 (1904).

[8] McMullen, THIS JOURNAL, **44**, 2060 (1922).

[9] Roux, *Ann. chim. phys.* [6] **12**, 330 (1887).

[10] Graebe, *Ann.*, **327**, 101 (1903).

This work was done under the direction of Professor F. B. Allan. The author held a Studentship from the Research Council of Canada.

Summary

1. Naphthalic anhydride or 4-bromonaphthalic anhydride cannot be used in place of phthalic anhydride in the Friedel and Crafts reaction.

2. Acenaphthene may be used in the Rubidge and Qua reaction for the preparation of phthalides from phthalic anhydride and aromatic hydrocarbons.

3. Many new derivatives of acenaphthene have been described.

TORONTO, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLII. A METHOD OF SYNTHESIZING 1,5-DIARYL-HYDANTOINS: 1,5-DI(PARA-HYDROXYPHENYL)-HYDANTOIN[1]

BY ROBERT D. COGHILL[2]

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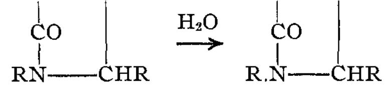
In a previous paper[3] on hydantoins, a description has been given of three of the four possible di-(*p*-phenol) derivatives of hydantoin the 1,3-diphenol, the 3,5-diphenol and the 5,5-diphenol. The synthesis and properties of the fourth representative of this series, the 1,5-diphenol, $\underbrace{\mathrm{NHCON(C_6H_4OH).CH(C_6H_4OH).CO}}$, are now described in this paper. I shall also report here the results of preliminary bacteriological tests carried out to determine the comparative antiseptic properties of several of these new phenolic derivatives.

The method of synthesis which was undertaken and applied successfully for the preparation of the diphenol-hydantoin is expressed by the formulas below.

$$\underset{\text{(Schiff Base)}}{\mathrm{RN{:}CHR}} + \mathrm{HCN} = \mathrm{RNH.CHR.CN}$$



$$\mathrm{RNH.CHR.CN + HCNO} \longrightarrow \begin{array}{l} \mathrm{NH_2\;\;CN} \\ \mathrm{\;|\;\;\;\;\;\;\;|} \\ \mathrm{CO\;\;\;\;|} \\ \mathrm{\;|\;\;\;\;\;\;\;|} \\ \mathrm{RN{-}{-}CHR} \end{array} \xrightarrow{H_2O} \begin{array}{l} \mathrm{NH{-}CO} \\ \mathrm{\;|\;\;\;\;\;\;|} \\ \mathrm{CO\;\;\;|} \\ \mathrm{\;|\;\;\;\;\;\;|} \\ \mathrm{R.N{-}{-}CHR} \end{array}$$

The Schiff base which served as the starting point of the synthesis was *p*-anisal-anisidine I. This is easily prepared by condensation of *p*-anisic aldehyde with *p*-anisidine or by the action of the latter amine on the cyano-

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[1] A contribution to the research on antiseptics conducted in coöperation with the National Research Council Sub-committee on "Internal Antisepsis."—T. B. Johnson, Chairman.

[2] Holder of the du Pont Fellowship in Chemistry, 1923–1924.

[3] Coghill and Johnson, THIS JOURNAL, **47**, 184 (1925).