esters, one of which was substituted by a crotyl and the other by an allyl group. No interchange of the migrating groups occurred.

BRYN MAWR, PENNSYLVANIA RECEIVED MARCH 27, 1941

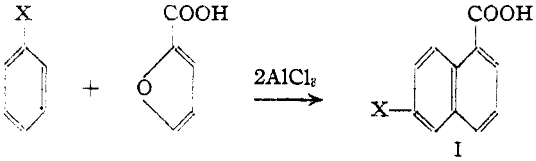
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of Furoic Acid with Aromatic Compounds*

BY CHARLES C. PRICE, E. C. CHAPIN, ARTHUR GOLDMAN, EDWIN KREBS AND H. M. SHAFER

In a search for a synthesis of certain naphthalene derivatives of known structure, the possibility of the application of the reaction of aromatic compounds with furoic acid in the presence of aluminum chloride has been investigated. Gilman, McCorkle and Calloway[1] have found that the acid obtained by King[2] from such a reaction of furoic acid with benzene was not phenyldihydrofuroic acid, but rather α-naphthoic acid, and McCorkle and Turck[3] have reported that toluene, anisole and chlorobenzene reacted similarly yielding the corresponding 6-substituted-1-naphthoic acids.

We have also isolated these products and have confirmed their structure, but in every case the yield of pure crystalline acid obtained was small (10–20%).



I
(10–20%)
(X = H, CH_3, OCH_3 or Cl)

The low yield of naphthoic acid has been accounted for, however, since we have found the major product of the reaction to be a mixture of higher molecular weight acids of complex structure, formed by the condensation of two or three molecules of the aromatic compound with one of furoic acid. The various naphthoic acids could be separated from these larger acids by extraction of the particular reaction mixture, after hydrolysis, with aqueous sodium bicarbonate. The high molecular weight acids were not extracted to any appreciable extent by this procedure although they were readily extracted by dilute sodium hydroxide.

From the reaction with benzene, the crude acid obtained from the bicarbonate extract contained about 30% α-naphthoic acid, the remainder consisting of a small amount (10–15%) of an amorphous acid and unreacted furoic acid. The α-naphthoic acid could be obtained from this mixture by recrystallization from toluene, or more satisfactorily by treatment with barium hydroxide. Barium α-naphthoate (and barium furoate) dissolved in hot water while the higher molecular weight acid formed an insoluble barium salt. The α-naphthoic acid (I, X = H) was identified by melting point and mixed melting point, by its neutral equivalent and by conversion to the anilide and to 5-bromo-1-naphthoic acid.

After removal of the naphthoic acid with bicarbonate, the high molecular weight acids were obtained readily by extraction with 2 to 5% sodium hydroxide. Acidification of such extracts yielded an amorphous powder which resisted all attempts at crystallization. On the basis of its analysis and neutral equivalent this material was a mixture which consisted principally of an acid formed by the condensation of three molecules of benzene with one of furoic acid, accompanied by the elimination of one molecule of water, contaminated with a similar product formed from two molecules of benzene and one of furoic acid. Decarboxylation of this mixture with copper chromite in quinoline gave a neutral oil in 50% yield which was readily dehydrogenated with sulfur to yield 22% of pure crystalline 1,4-diphenylnaphthalene, identified by analysis as well as by its melting point alone and admixed with an authentic sample.[4] The isolation of this hydrocarbon indicates that the product of the condensation of three molecules of benzene with one of furoic acid is 1,4-diphenyl-1,2,3,4-tetrahydro-1-naphthoic acid (III). This compound differs structurally from the α-naphthoic acid formed

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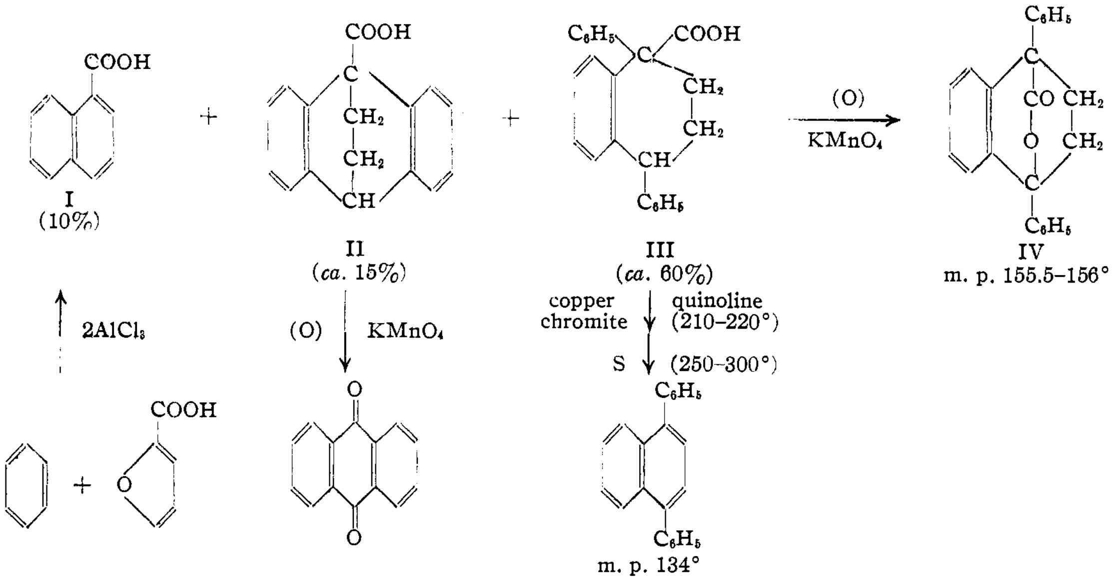
[1] Gilman, McCorkle and Calloway, THIS JOURNAL, **56**, 745 (1934); see also Calloway, *Chem. Rev.*, **17**, 343 (1935).

[2] King, THIS JOURNAL, **49**, 565 (1927).

[3] McCorkle and Turck, *Proc. Iowa Acad. Sci.*, **43**, 205 (1936).

[4] The authors are indebted to Dr. C. F. H. Allen for the authentic sample of 1,4-diphenylnaphthalene (Allen and Gilman, THIS JOURNAL, **58**, 937 (1936)).



simultaneously only in that two molecules of benzene have added to the two double bonds originally present in the furoic acid.

Oxidation of the crude high molecular weight acid with potassium permanganate gave small yields of three crystalline products. One, m. p. 155.5–156°, was obtained as a neutral substance, although originally soluble in the alkaline oxidation mixture. On the basis of its mode of formation and analysis, it is tentatively suggested that this compound is the lactone of 1,4-diphenyl-1,2,-3,4-tetrahydro-4-hydroxy-1-naphthoic acid (IV).

A second crystalline oxidation product has been identified as anthraquinone. The isolation of this compound indicates that the product formed by the condensation of two molecules of benzene with one of furoic acid is 9,10-*endo*-ethylene-9,10-dihydro-9-anthranoic acid (II). This substance is related structurally to the principal product (III) in that an *o*-phenylene group has replaced two phenyl groups.

The third crystalline oxidation product, m. p. 265–266°, is an acid of unknown structure.

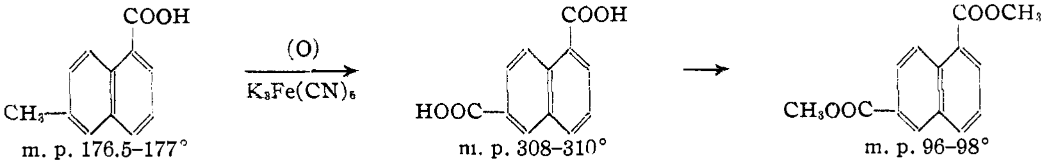
It would thus appear that the reaction of benzene with furoic acid yields at least three structurally related acids. One, α-naphthoic acid (I, X = H), formed by the condensation of one molecule of benzene with one of furoic acid, has been isolated in a pure crystalline condition. Two others, formed by condensation of two and three molecules of benzene with one of furoic acid, have been obtained as an amorphous mixture, characterized by neutral equivalent and analysis. The isolation of anthraquinone and 1,4-diphenylnaphthalene as degradation products of this material, as well as a consideration of the structure of the simplest product of the reaction, α-naphthoic acid, leads to the tentative suggestion that these latter two acids are 9,10-*endo*-ethylene-9,10-dihydro-9-anthranoic acid (II) and 1,4-diphenyl-1,2,3,4-tetrahydro-1-naphthoic acid (III), respectively.

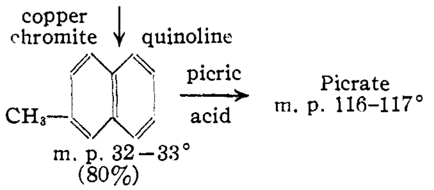
From either toluene or anisole the reaction with furoic acid produced a series of acids, apparently of similar structure, each with substituent methyl or methoxyl groups. From the reaction with toluene, for example, the naphthoic acid obtained had a methyl group in the 6-position (I, X = CH_3). The structure of this substance, which melted at 176.5–177°, was determined by oxidation to 1,6-naphthalic acid and by decarboxylation to β-methylnaphthalene.[5]

The high molecular weight acids obtained from the toluene and anisole reactions closely resembled the corresponding material from the benzene reaction in physical and chemical properties.

From toluene and methyl furoate the products obtained were the methyl esters of the acids formed directly from furoic acid and toluene. The isolation of 2,7-dimethylanthracene from this reaction lends support to the structure suggested for the acid of intermediate molecular weight (II).

(5) Weissgerber and Kruber (*Ber.*, **52**, 352 (1919)) have reported an acid, m. p. 150–152°, as 6-methyl-1-naphthoic acid. This material, prepared by the partial oxidation of a sample of 1,6-dimethylnaphthalene obtained from coal tar, must have been impure.





In the case of chlorobenzene, a better yield (18%) of the naphthoic acid, 6-chloro-1-naphthoic acid, was obtained. The position of the chlorine atom was indicated by the formation of β-chloronaphthalene on decarboxylation with copper chromite in quinoline. The yield of high molecular weight acid obtained from the sodium hydroxide extract of this reaction mixture was negligible.

One interesting property of the various high molecular weight acids is their solubility behavior, particularly in alkali. The acids dissolve readily in dilute aqueous sodium hydroxide, the solutions behaving much like soap solutions. On increasing the strength of the sodium hydroxide to 10% or even less, a viscous, heavy oil separates. This oil, which apparently must be the sodium salt since it dissolves in water, also dissolves readily in ether.

Experimental

The most satisfactory procedure for the purification of furoic acid was found to be through the methyl or ethyl ester. A mixture of 2400 g. of crude acid in 8 liters of methyl alcohol and 250 cc. of concentrated sulfuric acid was refluxed for six hours. Four liters of benzene and an equal volume of water was added and the aqueous layer, after dilution with water, was extracted with a second portion of benzene. The combined benzene extracts were washed with water and with sodium bicarbonate, dried and distilled; 1970 g. (73%) of methyl furoate, b. p. 76° (20 mm.); b. p. 180.5° (750 mm.); $n^{20}\text{D}$ 1.4875; $d^{20}{}_4$ 1.1792; $M^{20}\text{D}$ calcd. 30.07; $M^{20}\text{D}$ found 30.76,[6] was obtained. The ester reacted vigorously on warming with aqueous sodium hydroxide; 1670 g. (95%) of pure white crystals of furoic acid, m. p. 132–133°, separated on acidification and cooling in ice.

α-Naphthoic Acid.—Of a wide variety of procedures for carrying out the benzene–furoic acid reaction, the following gave the most satisfactory results and was used for a majority of the experiments. A suspension of 200 g. (1.78 moles) of pure furoic acid in 1500 cc. of thiophene-free benzene was cooled in an ice-bath and 500 g. (3.75 moles) of aluminum chloride was added in portions with stirring. After the addition was complete, the mixture was warmed gradually on a steam-plate to about 60° and stirred for twelve to eighteen hours. The dark red viscous reaction mixture was poured into cold aqueous hydrochloric acid and stirred vigorously at 60° until the tan cake formed on first contact with the water was entirely dissolved (about six to eight hours was required). The clear red benzene layer was separated and washed once with water. Thorough extraction with two portions of sodium bicarbonate yielded, on acidification, about 150 g. of crude acid, neut. eq. 215 to 230, from which a total of about 20–30 g. (7–10%) of pure α-naphthoic acid could be obtained by recrystallization from toluene. A quicker and more convenient method for obtaining a better yield of the pure acid (30–40 g.) was by treatment of a hot aqueous solution of the sodium salt of the crude material with barium hydroxide; the dark brown, higher-molecular weight acid was precipitated and the mother liquor, on acidification with hydrochloric acid and cooling, yielded α-naphthoic acid, m. p. 160–161° (160°).[7] The acid was identified by mixed melting point, by neutral equivalent, by conversion to the anilide, m. p. 164–164.5° (160°)[7], and to 5-bromo-1-naphthoic acid, m. p. 255–257° (262°),[8] neut. eq. 245 (calcd. 251).

1,4-Diphenyl-1,2,3,4-tetrahydro-1-naphthoic Acid (III).—After the bicarbonate extraction above, the benzene solution was extracted with 2% sodium hydroxide to yield about 300 g. of acid, neut. eq. 285 to 305, which could be obtained as a nearly colorless amorphous powder softening to a viscous oil at 80–100°. The glassy solid obtained on cooling the melt closely resembled rosin in physical appearance. It was very soluble in solvents such as benzene, alcohol, acetic acid, ether, chloroform, and toluene and resisted all attempts at crystallization. The analytical data indicated that this material was a mixture consisting principally of an acid formed by the condensation of three molecules of benzene with one of furoic acid with the elimination of water.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.09; H, 6.15; neut. eq., 328. Found: C, 83.32; H, 6.23; neut. eq., 306.5.

This acid (10 g.) was decarboxylated by heating at 210–220° in 75 cc. of quinoline in the presence of copper chromite for five hours. The neutral product (5 g. of acid was recovered) was a viscous oil (4.3 g.) which evolved hydrogen sulfide readily on heating with sulfur at 250 to 300°. The crystalline distillate from this dehydrogenation was recrystallized from alcohol to yield 1 g. of **1,4-diphenylnaphthalene** melting sharply at 134°.[9] The hydrocarbon was identified further by analysis and mixed melting point.[4]

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[6] Von Auwers (*Ber.*, **44**, 3689 (1911)) has reported the properties of this ester as b. p. 168°, $n^{20.6}\text{D}$ 1.48468, $d^{20}{}_4$ 1.1682, $M^{20}\text{D}$ calcd. 30.07, $M^{20}\text{D}$ found 30.90.

[7] Hofmann, *Ber.*, **1**, 39 (1868).

[8] Shoesmith and Rubli, *J. Chem. Soc.*, 3098 (1927).

[9] Weiss and Abeles (*Monatsh.*, **61**, 162 (1932)) report 135–137°, Allen and Gilman (THIS JOURNAL, **58**, 937 (1936)), 134–136°, and Dufraisse and Priou (*Bull. soc. chim.*, (5) **5**, 611 (1938)), 135–136°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.50; H, 6.08.

Oxidation of III.—The crude high-molecular weight acid from the sodium hydroxide extraction above was oxidized readily by aqueous alkaline potassium permanganate. In one experiment, a sample of 10 g. of acid in 100 cc. of 2% sodium hydroxide was stirred with 40 g. of potassium permanganate for one day at room temperature and then for one day on the steam cone. The manganese dioxide was collected by filtration and was dissolved by passing sulfur dioxide through its aqueous suspension. A pale yellow solid (0.85 g.) which remained undissolved was recrystallized from alcohol to yield **anthraquinone**, m. p. 278–280°, identified by mixed melting point and a vat test. The formation of small amounts of anthraquinone, as well as the discrepancies in the neutral equivalents and analyses for the crude samples of the acid, can be accounted for by the presence of **9,10-*endo*-ethylene-9,10-dihydro-9-anthranoic acid (II)**.

From a similar oxidation experiment using 35 g. of potassium permanganate, 0.45 g. of anthraquinone was isolated. Acidification of the oxidation mixture yielded about 2 g. of a bright yellow amorphous acid. This material could not be crystallized but when its ether solution was extracted with sodium bicarbonate and with potassium carbonate, a neutral residue remained in the ether. This compound crystallized from alcohol slowly as cubes; yield, 0.2 g., m. p. 155.5–156°. Its mode of formation and analysis suggest that its structure may be that of the **lactone** of **1,4-diphenyl-4-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid.**

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.63; H, 5.56. Found: C, 84.96; H, 5.74.

6-Methyl-1-naphthoic Acid.—A mixture of 400 cc. of toluene and 48 g. of furoic acid was stirred in an ice-bath while 120 g. of aluminum chloride was added in portions. The mixture was then warmed overnight on a steam-plate at about 60°. The hydrolysis was carried out in the same manner as for the benzene reaction described above. The sodium bicarbonate extract gave 10 g. of crystalline acid which, on recrystallization from benzene, yielded 6–7 g. (10%) of white plates of **6-methyl-1-naphthoic acid,** m. p. 176.5–177°.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.39; H, 5.42; neut. eq., 186. Found: C, 77.31; H, 5.71; neut. eq., 180, 181.

The acid was further characterized by conversion to the **anilide,** which formed slender needles from benzene, m. p. 167–168°.

Anal. Calcd. for $C_{18}H_{15}NO$: N, 5.36. Found: N, 5.37, 5.61.

Oxidation of the acid above with potassium ferricyanide[10] yielded a second acid, m. p. 308–310°, which was esterified with methyl alcohol and sulfuric acid; the ester melted at 96–98°. These properties correspond to **1,6-naphthalic acid** (m. p. 310°) and its **dimethyl ester** (m. p. 99°), respectively.[10]

Decarboxylation of 0.5 g. of the methylnaphthoic acid by heating for an hour and a half in 2 cc. of quinoline in the presence of 0.2–0.3 g. of copper chromite catalyst under an atmosphere of nitrogen proceeded smoothly at 200–205°. The reaction mixture was cooled, 25 cc. of ether was added, and the catalyst was removed by filtration. The solution was washed with dilute hydrochloric acid and with sodium bicarbonate. The dark red color in the ether was removed by treatment with charcoal and the pale orange ether solution was then evaporated, leaving 0.5 g. of an oil which crystallized at room temperature. This was dissolved in 10 cc. of hot alcohol and treated with 1 g. of picric acid. On cooling, 0.62 g. (64% over-all yield) of long orange-yellow needles of **β-methylnaphthalene picrate** separated, m. p. 116–117°. A mixture with an authentic sample (m. p. 116.5–117°)[11] showed no depression in melting point. The picrate was dissolved in 15 cc. of ether and decomposed by washing three times with dilute ammonia. Evaporation of the ether left a crystalline residue of **β-methylnaphthalene**, m. p. 32–33°. Mixed with an authentic sample (m. p. 34–35°),[11] it melted at 33–34°.

Attempted decarboxylation of 0.8 g. of the methylnaphthoic acid with 4 cc. of concentrated hydrochloric acid and 4 cc. of water at 220–225° for twelve hours according to the procedure used by Weissgerber and Kruber[5,10] failed; 0.6 g. of the starting material was the only product isolated.

Similar treatment of 1 g. of α-methylnaphthalene yielded 0.95 g. of an oil which was identified as the starting material by treating with picric acid in alcohol; 1.9 g. of orange needles of α-methylnaphthalene picrate was obtained, m. p. 142–143.5°. Mixed with an authentic sample (m. p. 143–144°)[12] there was no depression in the melting point. This would apparently eliminate the possibility that the β-methylnaphthalene obtained by Weissgerber and Kruber[5] from the acid they believed to be 6-methyl-1-naphthoic acid could have been formed by migration of a methyl group.

1,4-Ditolyl-6-methyl-1,2,3,4-tetrahydro-1-naphthoic Acid.—Extraction of the furoic acid–toluene reaction mixture above with 2% sodium hydroxide gave 105 g. (68%) of an acid, very similar in appearance and properties to the homolog from benzene. Values for the molecular weight of this substance, determined ebullioscopically in benzene, varied from 365 to 410.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.27; H, 7.08; neut. eq., 370. Found: C, 82.23; H, 7.12; neut. eq., 345.

Methyl 6-Methyl-1-naphthoate.—When a solution of methyl furoate in toluene was treated with aluminum chloride, hydrogen chloride was evolved when the reaction was carried out at 0–10° or at 80–90°. In one experiment, 22.3 g. (0.2 mole) of methyl furoate in 125 cc. of toluene was treated with 53.4 g. (0.4 mole) of aluminum chloride with stirring in an ice-bath. The mixture was kept at room temperature for six hours and at 80–90° for another six hours. During this period the reaction mixture became dark red. The complex was decomposed with ice water and hydrochloric acid, ether was added and the toluene layer washed with hydrochloric acid, sodium bicarbonate and water. After removal of ether and toluene, there remained 50 cc. of dark oil which was fractionally distilled. The fraction boiling from 102–120° (2 mm.) (155–165° (17 mm.)), 3.2 g. (8%), consisted chiefly of **methyl 6-methyl-1-naphthoate,** as shown by saponification with 20% potassium hydroxide to 6-methyl-1-naphthoic acid. The

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[10] Weissgerber and Kruber, *Ber.*, **52**, 352 (1919).

[11] Ciamician, *ibid.*, **11**, 272 (1878).

[12] Meyer and Fricke, *ibid*, **47**, 2770 (1914).

boiling point rose gradually to 250° and still a large proportion of the mixture remained undistilled as a dark red oil. Saponification of this residue yielded an acid which appeared to be identical with the amorphous high molecular weight acid obtained directly from furoic acid and toluene.

From all these reactions with toluene, the distillate boiling at about 160–200° (2 mm.) yielded a small amount of **2,7-dimethylanthracene,** m. p. 240–241° (241°).[13]

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84; mol. wt., 206. Found: C, 92.88; H, 7.34; mol. wt., 212, 205.

It was identified by conversion to the quinone with chromic acid in acetic acid. The hydrocarbon (60 mg.) yielded 50 mg. of pale yellow needles of **2,7-dimethylanthraquinone,** m. p. 169–170° (170°).[13]

A better yield of methyl 6-methyl-1-naphthoate was obtained using carbon disulfide, rather than excess toluene, as a solvent. When a solution of 10 g. of methyl furoate and 10 g. of toluene in 100 cc. of carbon disulfide was treated with 26 g. of aluminum chloride, the reaction proceeded with sufficient vigor to boil the solvent. A dark red complex separated from the solution. After ten hours the mixture was decomposed with ice and hydrochloric acid. The organic layer was washed with hydrochloric acid, with sodium bicarbonate and with water; it was then dried and distilled. The fraction boiling up to 124° (2 mm.) (4.3 g.) was redistilled to yield 3.3 g. (18%) of **methyl 6-methyl-1-naphthoate;** b. p. 110–114° (2 mm.); $n^{20}D$ 1.5795. A small portion of higher boiling material was **2,7-dimethylanthracene** and an appreciable residue remained undistilled at 265° (2 mm.).

6-Methoxy-1-naphthoic Acid.—A mixture of 12 g. of furoic acid and 100 cc. of anisole was treated with 30 g. of aluminum chloride in portions with stirring. After the addition was complete the mixture was stirred for eighteen hours on a steam plate and then poured into aqueous hydrochloric acid. When the hydrolysis was complete, ether was added and the mixture was extracted with sodium bicarbonate to give 6.5 g. of crude acid (neut. eq. 263). This material was recrystallized from benzene to give 2.5 g. (12%) of **6-methoxy-1-naphthoic acid** as white plates, m. p. 180–180.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.25; H, 4.99; neut. eq., 202. Found: C, 71.20; H, 5.02; neut. eq., 207.

1,4-Dimethoxyphenyl-6-methoxy-1,2,3,4-tetrahydro-1-naphthoic Acid.—Acidification of the 2% sodium hydroxide extract of the reaction mixture above yielded 20 g. of a pale amorphous acid. This material absorbed no hydrogen on shaking in alcohol in the presence of Raney nickel under three atmospheres pressure.

Anal. Calcd. for $C_{26}H_{26}O_5$: C, 74.60; H, 6.27; neut. eq., 418. Found: C, 73.93; 73.99; H, 6.33, 6.32; neut. eq., 436.

6-Chloro-1-naphthoic Acid.—In an experiment identical with the one above except that chlorobenzene was used in place of anisole, the sodium bicarbonate extract weighed 7 g. (no other acid could be obtained by extraction with 2 or 5% sodium hydroxide). Recrystallization from benzene yielded 3.5 g. (18%) of 6-chloro-1-naphthoic acid, m. p. 188–189°.

Anal. Calcd. for $C_{11}H_7O_2Cl$: C, 63.92; H, 3.42; neut. eq., 206.5. Found: C, 64.04; H, 3.45; neut. eq., 202.

This acid (2 g.) was decarboxylated by heating at 225° in 10 cc. of quinoline with copper chromite catalyst for four hours. Ether was added to the cool mixture and the solution was extracted with hydrochloric acid and with sodium bicarbonate. From the latter, 1.5 g. of starting material was recovered. The ether solution was treated with charcoal and evaporated; the crystalline residue was recrystallized from methanol to yield 0.2 g. of white plates of **β-chloronaphthalene,** m. p. 58–59°.[14]

Summary

α-Naphthoic acid and 6-methyl-, 6-chloro- and 6-methoxy-1-naphthoic acids have been isolated in yields of 10–20% from the reaction of benzene, toluene, chlorobenzene and anisole, respectively, with furoic acid in the presence of aluminum chloride. Of these acids, only α-naphthoic acid has been previously characterized in the literature.

With the exception of the reaction with chlorobenzene, the principal products, however, were found to be mixtures of amorphous acids of higher molecular weight. From benzene, this material yielded 1,4-diphenylnaphthalene on decarboxylation and dehydrogenation; one constituent of this mixture must therefore be 1,4-diphenyl-1,2,3,4-tetrahydro-1-naphthoic acid.

Since the high molecular weight acids may be readily separated from the naphthoic acids, this reaction may serve as a convenient method for the synthesis of certain substituted naphthoic acids not readily available by the usual methods.

URBANA, ILLINOIS RECEIVED MARCH 17, 1941

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[13] Morgan and Coulson, *J. Chem. Soc.*, 2203 (1929).

[14] Liebermann and Palm (*Ann.*, **183**, 270 (1876)) report 61°, Heumann and Kochlin (*Ber.*, **16**, 1627 (1883)), 60°, and Roux (*Ann. chim.*, [6] **12**, 349 (1888)), 58°.