

Toward carbonate and hydroxide solutions the compound behaves like the 1-phenyl-3-benzoylamino-5-pyrazolone.

**1-Phenyl-3-acetylamino-5-acetoxypyrazole.**<sup>4</sup>—A solution of 8.75 g. of 1-phenyl-3-amino-5-pyrazolone in 50 ml. of acetic anhydride was refluxed for half an hour. After decomposing the mixture in 250 ml. of water, the product was filtered off and recrystallized from 90 ml. of toluene; 8 g. (62%) of fine, cream colored crystals; m. p. 144–145°.

*Anal.* Calcd. for  $C_{13}H_{13}N_3O_3$ : N, 16.22. Found: N, 16.12.

The compound is insoluble in 3% sodium carbonate. It dissolves in cold 2% sodium hydroxide with saponification of one acetyl group; on acidification with acetic acid 1-phenyl-3-acetylamino-5-pyrazolone is obtained; m. p. and mixed m. p. 218–220°.

**1-Phenyl-3-phenylcarbamiylamino-5-pyrazolone.**—To a hot solution of 5 g. of 1-phenyl-3-amino-5-pyrazolone in 20 ml. of dioxane was added 3.4 g. of phenyl isocyanate and the mixture heated for two hours on the steam-bath. The product which crystallized on cooling was purified by stirring with 25 ml. of ethanol; 2.3 g. (28%) of pure white microcrystals, m. p. 235–236°.

*Anal.* Calcd. for  $C_{16}H_{14}N_4O_2$ : N, 19.0. Found: N, 19.00.

Toward carbonate and hydroxide solutions the compound behaves like the 1-phenyl-3-benzoylamino-5-pyrazolone.

**1-Phenyl-3-anilino-5-pyrazolone.**—A mixture of 20 g. of 1-phenyl-3-amino-5-pyrazolone<sup>7</sup> and 50 ml. of aniline was refluxed gently over a flame for one and one-half hour,

*i. e.*, until the evolution of ammonia slacked off. After some cooling, 100 ml. of chloroform was added and the solution cooled in an ice-bath. The product (14.6 g.) was recrystallized from 300 ml. of 95% ethanol, filtering hot from a small amount of insoluble yellow material; 12 g. (43%) of white, feathery needles, m. p. 219–221°.

*Anal.* Calcd. for  $C_{15}H_{13}N_3O$ : N, 16.70. Found: N, 16.77.

The compound is sparingly soluble in cold 3% sodium carbonate, but soluble in cold 2% sodium hydroxide, from which it separates unchanged on acidification.

### Summary

1. 1-Phenyl-3-amino-5-pyrazolone was prepared, starting with the ethyl ester of 1-phenyl-3-carboxy-5-pyrazolone, by way of the corresponding hydrazide and azide and Curtius degradation of the latter.

2. The reaction product is identical with the compound prepared by Conrad and Zart<sup>1</sup> from ethyl cyanoacetate and phenylhydrazine and formulated as 1-phenyl-3-hydroxy-5-pyrazolone imide.

3. The compound prepared by Conrad and Zart is, therefore, 1-phenyl-3-amino-5-pyrazolone.

4. A number of derivatives of 1-phenyl-3-amino-5-pyrazolone were prepared.

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

## The Reaction of Methyl Furoate with Benzene and Chlorobenzene

BY CHARLES C. PRICE AND C. F. HUBER

The aluminum chloride-catalyzed reaction of furoic acid with benzene has been found to yield, in addition to  $\alpha$ -naphthoic acid,<sup>1</sup> a large amount of an amorphous mixture of acids of higher molecular weight.<sup>2</sup> Although some suggestions as to the nature of certain components of this material were advanced on the basis of degradation products of the crude mixture, the isolation of any pure acids has proved extremely difficult. Since attempts at fractional crystallization or precipitation of the acids or of various derivatives were so generally unsuccessful, the condensation reaction has been investigated employing methyl furoate in place of furoic acid, with the aim of separating by distillation the esters so formed.

(1) Gilman, McCorkle and Calloway, *THIS JOURNAL*, **56**, 745 (1934).

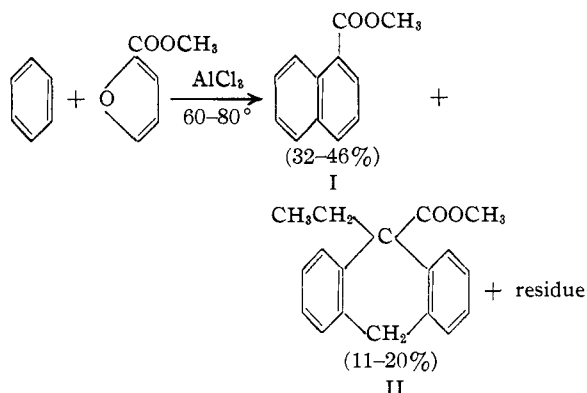
(2) Price, Chapin, Goldman, Krebs and Shafer, *ibid.*, **63**, 1857 (1941).

McCorkle and Turck<sup>3</sup> were able to isolate a 56% yield of methyl  $\alpha$ -naphthoate from the aluminum chloride-catalyzed reaction of methyl furoate with benzene, and Calloway<sup>4</sup> reported that a considerable residue remained after distillation of the naphthoate. We have obtained the same results, isolating methyl  $\alpha$ -naphthoate in 32–46% yield accompanied by a residue of higher-boiling products.

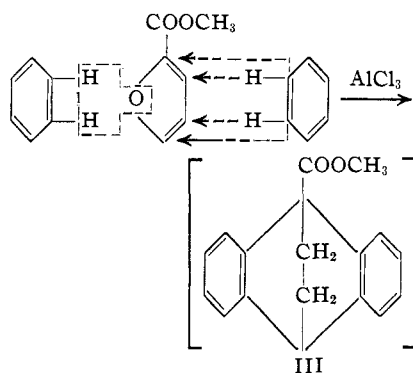
Fractional distillation of this residue under the vacuum of a mercury vapor pump yielded a pale yellow, viscous oil, boiling at 144–145° (0.04 mm.), which crystallized after standing for seven months, m. p. 52–54°. The yield of this substance, which proved to be methyl 9-ethyl-9,10-dihydro-9-anthroate (II), corresponded to 11–20% of the theoretical amount.

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

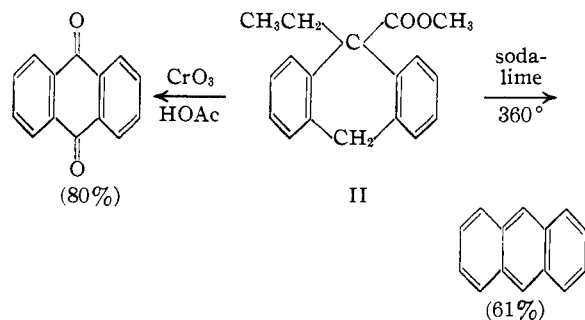
(4) Calloway, *Chem. Rev.*, **17**, 343 (1935).



A product of this nature, containing an anthracene nucleus, had been expected on the basis of the previously reported isolation of anthraquinone from the permanganate oxidation of the crude high-molecular-weight acids from the benzene-furoic acid reaction.<sup>2</sup> We had anticipated, however, that its structure would be that of methyl 9,10-*endo*-ethano-9,10-dihydro-9-anthroate (III). Such a compound could be pictured as having been formed by the addition of an *o*-phenylene group across the two double bonds originally present in the furoic acid ring.

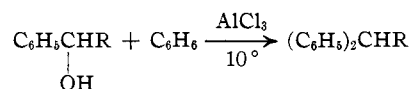


The crystalline ester (II) actually isolated, however, analyzed consistently for a substance with a molecular formula containing two more hydrogen atoms than the expected *endo*-ethano anthroate, III. If III actually is formed as an

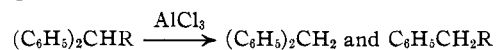


intermediate, its anthracene nucleus is not destroyed by the addition of these two hydrogen atoms, however, since II could be converted to anthraquinone in 80% yield by chromic acid oxidation and to anthracene in 61% yield by soda-lime distillation.

The apparent scission of the *endo*-ethano ring of III to give II is closely analogous to some experiments recorded by Huston and Friedeman.<sup>5</sup> These authors found that treatment of  $\alpha$ -phenylethyl or  $\alpha$ -phenylpropyl alcohols with benzene and aluminum chloride led principally to the expected product, the 1,1-diphenylalkane.

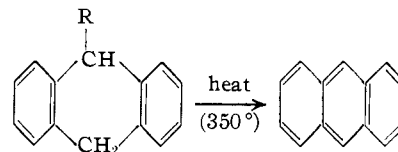


As the temperature of the reaction mixture was raised to 25°, increasing amounts of diphenylmethane were isolated. The authors expressed the opinion that the source of this material was the catalytic cleavage of the original condensation product.



The analogy of this cleavage to that postulated above for conversion of III to II is very close since the two end rings of the anthracene nucleus correspond to the two phenyl groups in the 1,1-diphenylalkanes and the *endo*-ethano group of the former corresponds to the alkyl group of the latter.

Precedent for the loss of the ethyl as well as the carboxyl group during the soda-lime distillation is to be found in some observations of Liebermann,<sup>6</sup> who found that several 9-alkyl-9,10-dihydroanthracenes were converted to anthracene by heat.

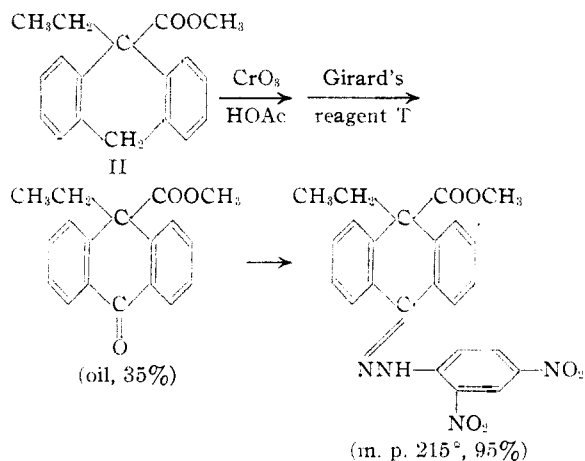


Cleavage of the *endo*-ethano ring to give an ethyl group in the 9-position, rather than an ethyl group in the 10-position or methyl groups in the 9- and 10-positions, follows from the ready oxidation of II to a ketone. Only the 9-ethyl derivative would contain an active methylene group necessary for this conversion.

Substantiation for this location of the ethyl group may be derived from the stability of the

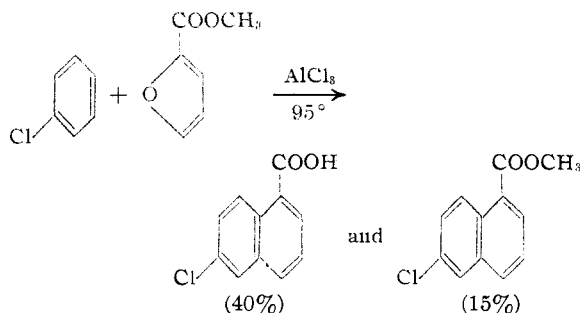
(5) Huston and Friedeman, *THIS JOURNAL*, **40**, 785 (1918).

(6) Liebermann, *Ann.*, **212**, 76 (1882).



ester (II) toward hydrolysis: even saponification in boiling diethylene glycol failed. Of the three possible modes of cleavage of the *endo*-ethano ring, that forming the 9-ethyl derivative would yield the compound with a maximum of steric hindrance to reactions of the ester group.

When the reaction of methyl furoate with chlorobenzene was carried out by exactly the same procedure as that employed for the reaction with benzene, with the exception that the condensation was carried out at 95° rather than 70°, a 40% yield of 6-chloro-1-naphthoic acid was isolated by acidification of the sodium bicarbonate wash liquor. Only a small amount of neutral product remained in the chlorobenzene layer; this consisted principally of methyl 6-chloro-1-naphthoate (15%). The reaction thus differed in two essentials from that with benzene: (1) the ester group was largely cleaved to a carboxyl group and (2) no significant amount of higher molecular weight material was formed. In this latter respect the reaction corresponds to that of furoic acid with chlorobenzene. The yield of chloronaphthoic acid from methyl furoate was nearly three times that from furoic acid.



Thus, for both benzene and chlorobenzene, condensation to form a naphthalene nucleus seems to

be far more satisfactory with methyl furoate than with furoic acid.

### Experimental

**Methyl Furoate plus Benzene.**—Methyl furoate (125 g., 1.1 mole) and 625 cc. of dry benzene (thiophene-free and dried over sodium) were cooled in an ice-bath and treated with anhydrous aluminum chloride (267 g., 2.0 moles) at 0°. After the reaction mixture had been stirred at room temperature for two hours, it was heated in an oil-bath at 70° for thirty hours. The dark red-black mixture was poured into ice and hydrochloric acid and stirred for two hours at room temperature to ensure hydrolysis of the aluminum chloride complex. The layers were separated, and the benzene solution was washed once with dilute hydrochloric acid, twice with saturated sodium bicarbonate solution and finally with water. The solution was dried over anhydrous magnesium sulfate, the benzene was removed by distillation, and 250 cc. of a dark oil was obtained. This oil was distilled under reduced pressure and two fractions were obtained: I, methyl  $\alpha$ -naphthoate (80 g., 43%) b. p. 100–102° (0.04 mm.),  $n_D^{20}$  1.6068,  $d_4^{20}$  1.129; and II, methyl 9-ethyl-9,10-dihydro-9-anthrate, a pale yellow viscous oil (53 g., 20%) b. p. 144–145° (0.04 mm.),  $n_D^{20}$  1.5931; after standing for seven months this oil finally crystallized, m. p. 52–54°.

*Anal.* Calcd. for  $C_{18}H_{16}O_2$ : C, 81.17; H, 6.80; mol. wt., 266. Found: C, 81.18; H, 6.72; mol. wt., 264, 268.

The residue could not be distilled and when the temperature of the heating bath was raised above 275° it began to decompose, making it impossible to maintain the diminished pressure.

The methyl  $\alpha$ -naphthoate was characterized by saponification; 20 g. (0.11 mole) and 150 cc. of 25% potassium hydroxide were placed in a flask and refluxed overnight (twenty hours). The mixture was then cooled, diluted with an equal amount of water and neutralized with dilute hydrochloric acid. Seventeen and one-half grams (95%) of  $\alpha$ -naphthoic acid was obtained, which was crystallized from 95% ethanol, m. p. 160–161°. The  $\alpha$ -naphthoic acid was further characterized by conversion to the amide by treatment with thionyl chloride followed by ice-cold aqueous ammonia, m. p. 204–205°.

**Reaction of II with Soda Lime.**—Eight grams (0.03 mole) of II was placed in a distilling flask with 15 g. of soda lime. The flask was heated to slightly above 360° for three-quarters of an hour. It was then set for distillation *in vacuo* and the pressure reduced to 2 mm. An oil distilled which immediately crystallized, yielding 3.3 g. (61%) of anthracene, m. p. 211–212°. Mixed with an authentic sample of anthracene melting at 212–213° it gave a melting point of 211–212°. The hydrocarbon was further characterized by the formation of its picrate, m. p. 136–137°.

**Oxidation of II to Anthraquinone.**—Five grams (0.019 mole) of II was dissolved in 60 cc. of glacial acetic acid. The solution was stirred while chromic anhydride (12.5 g., 0.125 mole) dissolved in 15 cc. of water and 25 cc. of acetic acid was added slowly from a dropping funnel. It was stirred for three hours longer at room temperature and then poured into 400 cc. of ice-water. A precipitate of anthraquinone (3.2 g., 80%) was obtained. This was crystal-

lized from ethanol, m. p. 268–269°. Mixed with an authentic sample, m. p. 272–273°, it melted at 270–271°. The quinone was further characterized by preparing the derivative with phenylhydrazine, m. p. 180–181°.

**Oxidation of II to the Ketone.**—Six grams (0.023 mole) of II was dissolved in 75 cc. of glacial acetic acid and cooled to about 10°. The solution was stirred vigorously while 3 g. (0.031 mole) of chromic anhydride, dissolved in 10 cc. of water and 10 cc. of acetic acid, was added slowly. The cooling-bath was then removed and the reaction mixture stirred at room temperature for three-quarters of an hour. It was poured into ice-water (200 cc.) yielding an oil which was extracted with benzene. The benzene solution was washed with sodium bicarbonate solution followed by water. The solvent was evaporated leaving an oil (5.6 g., 90%). This crude ketone was purified by the use of betainehydrazide hydrochloride (Girard's reagent T). The oil was dissolved in 125 cc. of absolute ethanol, to which was added 8.4 g. (0.05 mole) of Girard's reagent T and 12 cc. of glacial acetic acid. The mixture was refluxed for one hour, cooled and poured into 900 cc. of ice-water containing enough sodium hydroxide to neutralize nine-tenths of the acetic acid. The solution was then acid to brom thymol blue indicator. The water solution was extracted three times with 125-cc. portions of benzene, then acidified with enough concentrated hydrochloric acid to make the entire solution 0.5 normal, and allowed to stand overnight. It was again extracted with benzene (250 cc. in three portions). The benzene solution was washed with sodium bicarbonate, followed by water. The benzene was evaporated, yielding 2 g. (35%) of pale, viscous oily ketone. From this material a 2,4-dinitrophenylhydrazone was prepared by refluxing in alcohol solution. Crystals began to separate in a few minutes; yield, 3.1 g. (95%). After crystallization from alcohol and ethyl acetate, the bright red crystals melted sharply at 215°.

*Anal.* Calcd. for  $C_{22}H_{20}O_6N_4$ : C, 62.60; H, 4.35; N, 12.18. Found: C, 62.72; H, 4.34; N, 12.32.

**Reaction of Methyl Furoate and Chlorobenzene.**—Seventy-five grams (0.6 mole) of methyl furoate dissolved

in 500 cc. of chlorobenzene was cooled to 0° in an ice-bath. The solution was stirred and 162 g. (1.2 mole) of anhydrous aluminum chloride was added over a period of thirty minutes. The stirring was continued for thirty minutes at 0°, for one and one-half hours at room temperature and finally for twenty-eight hours at 90–100°. The reaction mixture was then poured into a mixture of ice and hydrochloric acid and stirred for three hours at room temperature. The mixture emulsified badly and one liter of ether was added to facilitate the separation. The ether layer was washed with dilute hydrochloric acid, with water, three times with saturated sodium bicarbonate, and finally with water. It was then dried over anhydrous magnesium sulfate and the ether removed by evaporation. The residue was placed in a modified Claisen flask and distilled; 20 g. (15%) of methyl 6-chloro-1-naphthoate was obtained, b. p. 165–170° (2 mm.).

The sodium bicarbonate extract was acidified with hydrochloric acid and 53 g. (44%) of crude 6-chloro-1-naphthoic acid was obtained. This was recrystallized once from 95% ethanol and once from benzene, yielding 46 g. (39%) of 6-chloro-1-naphthoic acid, m. p. 188–189°.

### Summary

The aluminum chloride-catalyzed reaction of methyl furoate with benzene has been found to yield methyl  $\alpha$ -naphthoate in 32–46% yield while chlorobenzene was converted to 6-chloro-1-naphthoic acid in good yield. Esterification of furoic acid thus appears to favor this condensation to a naphthalene derivative.

In addition to methyl  $\alpha$ -naphthoate, the reaction with benzene yielded a higher boiling product in 11–20% yield. Evidence has been presented indicating that this compound is methyl 9-ethyl-9,10-dihydro-9-anthroate.

URBANA, ILLINOIS

RECEIVED APRIL 14, 1942

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

## A Study of the Products Obtained from Starch by the Action of the Amylase of *Bacillus macerans*

BY W. S. McCLENAHAN, EVELYN B. TILDEN AND C. S. HUDSON

Preliminary experiments on the conversion of potato starch to the crystalline Schardinger dextrans by *Bacillus macerans* showed that the action was produced by a new type of amylase present in bacteria-free filtrates of the cultures.<sup>1</sup> In this paper we wish to report precise data on the nature and extent of the changes in optical rotation,<sup>2</sup> vis-

(1) (a) Tilden and Hudson, *THIS JOURNAL*, **61**, 2900 (1939); (b) Tilden and Hudson, *J. Bact.*, **43**, 527 (1942).

(2) In the preliminary publication it was reported that there was no significant change in rotation during digestion, but we now find under more exact test that the change is of considerable magnitude, as shown in Fig. 3.

cosity and reducing action occurring during digestion of various starch samples by purified concentrates<sup>3</sup> of the *macerans* amylase, and to record the yields of alpha and beta dextrans obtainable. Also, the crystalline alpha and beta dextrans have been purified, their constants determined, and their stability toward *macerans* amylase studied.

When *macerans* amylase was allowed to act for one month upon a 2% suspension of potato

(3) Tilden, Adams and Hudson, *THIS JOURNAL*, **64**, 1432 (1942).