[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Behavior of *o*-Aroylbenzoic Acid Types in Acidic Media[1]

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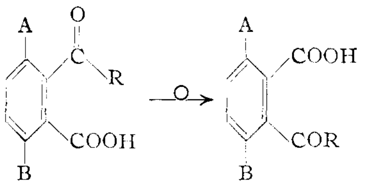
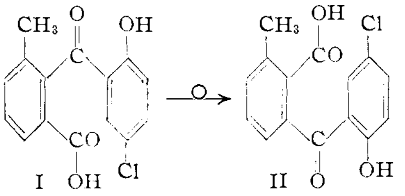
We show that 3-nitro-2-(2-thenoyl)-benzoic acid (III) rearranges to 6-nitro-2-(2-thenoyl)-benzoic acid (IV) in 100% sulfuric acid at 70°, contrary to two previous reports of other results. A probable reason for the previous reports is advanced. Trifluoroacetic acid, methanesulfonic and polyphosphoric acid are shown to be unsuitable acidic reagents for effecting the rearrangement of III to IV. Both 4-nitro-2-(2-thenoyl)-benzoic acid (VI) and 5-nitro-2-(2-thenoyl)-benzoic acid (VII) are recovered unchanged on treatment with 100% sulfuric acid at 70° whereas at higher temperatures (140–170°) the same mixture of about equal amounts of 7-nitro- and 6-nitrothiophanthraquinones (VIII and IX) is formed starting from either VI or VII. On heating 1-(2-thenoyl)-2-naphthoic acid (XI) in 100% sulfuric acid at 60° 2-(2-thenoyl)-1-naphthoic acid (X) is formed, whereas the rearrangement of X to XI does not occur. At higher temperatures both X and XI are converted to the same mixture of about 60% of 5,6-benz-4,9-thiophanthraquinone (XII) and 40% of 7,8-benz-4,9-thiophanthraquinone (XIII). A mechanism which allows the above facts to be understood is presented. In addition observations on the esterification of the keto acids involved are given.

The work herein reported was undertaken because of our general interest in the chemistry of *o*-benzoylbenzoic type acids and anthraquinone formation in solutions of sulfuric acid. Three main topics will be treated: the rearrangement of *o*-benzoylbenzoic type acids, the formation of anthraquinone type compounds and the esterification of *o*-benzoylbenzoic type acids.

Several instances of the rearrangement involving the following types of acid, where R is an aryl or thienyl group, are known to occur on treatment with sulfuric acid.



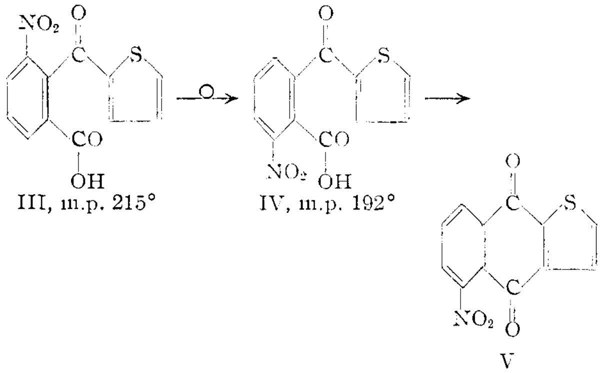
The first case, I → II, was discovered[3] in 1927. Several other examples have since been reported.[4–7]



I II

Closely related to this phenomenon is the fact that certain *o*-aroylbenzoic acids yield anthraquinone type products which could have arisen only from a rearranged acid, *e.g.*, 2-carboxy-di-1-naphthyl ketone yields 1,2,5,6-dibenzanthraquinone.[8] Further examples of this type of rearrangement have been reported.[8,9]

Because of conflicting claims,[6,9] we chose to reinvestigate the behavior of 3-nitro-2-(2-thenoyl)-benzoic acid (III), and 6-nitro-2-(2-thenoyl)-benzoic acid (IV) in sulfuric acid; IV was reported[6] to rearrange to III and III was reported[9] to rearrange to 3-nitro-2-(3-thenoyl)-benzoic acid. We have found that *III rearranges to IV* on heating in 100% sulfuric acid for 30 minutes[10] at 70°. Only unrearranged acid was obtained after heating III with trifluoroacetic anhydride for one day at reflux, with methanesulfonic acid at 100° for 5 hours or with polyphosphoric acid at 140° for 2 minutes, although in the latter case a 14% yield of 5-nitrothiophanthraquinone (V) was obtained. The latter finding will be discussed below.



III, m.p. 215° IV, m.p. 192° V

From our work it appears that the earlier workers[6,9] went astray because they assumed that the acid, m.p. 170°[11] (or 172–173°[6]), was pure 6-nitro-2-(2-thenoyl)-benzoic acid (IV), whereas we now show that pure IV melts at 191.0–192.0°. We believe that the lower melting acid obtained by the previous workers[6,9] was a mixture of III and IV or possibly a 1:1 molecular compound of III and IV. The acid, m.p. 188–190°, obtained by treating III with 100% sulfuric acid at 70–90° from 30 to 15 minutes[9] was in reality IV and not 3-nitro-2-(3-thenoyl)-benzoic acid as suggested. When the acid, m.p. 172–173°, supposedly IV, was heated at 60° for one hour with concentrated sulfuric acid, the acid III, m.p. 215–217°, was obtained.[6] We believe this result may be explained on the basis that the starting acid, m.p. 172–173°, assumed to be IV, was a mixture of III and IV, and that in the

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[1] The work herein presented formed part of the Ph.D. thesis, Ohio State University, 1957, presented by K. G. Ihrman. This work was supported in part by a grant from the du Pont Co.

[2] To whom inquiries should be addressed.

[3] M. Hayashi, *J. Chem. Soc.*, 2516 (1927).

[4] M. Hayashi, *ibid.*, 1513, 1520, 1524 (1930).

[5] M. Hayashi, *Bull. Chem. Soc., Japan*, **11**, 184 (1936).

[6] R. Goncalves, M. R. Kegelman and E. V. Brown, *J. Org. Chem.*, **17**, 705 (1952).

[7] R. B. Sandin, *et al.*, THIS JOURNAL, **78**, 3817 (1956).

[8] J. W. Cook, *J. Chem. Soc.*, 1472 (1932).

[9] H. E. Schroeder and V. Weinmayr, THIS JOURNAL, **74**, 4357 (1952).

[10] These experimental conditions were chosen because of the series of experiments reported on p. 4361 of ref. 9.

[11] V. Weinmayer, THIS JOURNAL, **74**, 4353 (1952).

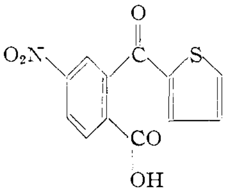
acid treatment, most of the IV was destroyed,[12] and hence III was isolated. This finding led to the statement that IV rearranges to III.[6]

The statement[9] that both III and IV lead to V is correct, as III rearranges to IV prior to cyclization. In the present case, the conditions of isomerization of III to IV are milder than those required to cyclize IV to V, hence we were able to show that in the cyclization of III to V in sulfuric acid, III first rearranges to IV which in turn is cyclized to V at higher temperatures. In the case of polyphosphoric acid cyclization of III to V mentioned above, the rearrangement of III to IV prior to formation of V could not be demonstrated as conditions drastic enough to isomerize III to IV are also sufficient to cause cyclization of IV to V.

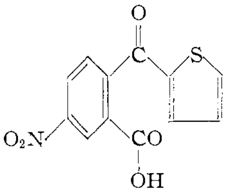
Our results with 4-nitro-2-(2-thenoyl)-benzoic acid (VI), and 5-nitro-2-(2-thenoyl)-benzoic acid (VII), also differ somewhat from those reported.[6,9] Compound VI was reported to yield VII on treatment with concentrated sulfuric acid[6] whereas we found that VI and VII are recovered unchanged from their solutions in sulfuric acid.

In another aspect of this work VI and VII were said[9] to form mainly 7-nitrothiophanthraquinone (VIII) on heating with aluminum chloride in nitrobenzene at 130° for 20 hours.[9] The authors commented on the difficulty of establishing the composition of the nitroquinone mixtures obtained. We have determined that on cyclization of VI with 100% sulfuric acid at 170° for 3 minutes (22% yield) or of VII at 140° for 2 minutes (52% yield) the *same mixture of about equal amounts of VIII and IX is obtained.* The determinations were based on conversion to the corresponding chloroquinones followed by comparison of X-ray powder photographs. Although the cyclizations were carried out with a different acidic medium than ours, we believe that the products obtained by Schroeder and Weinmayr[9] may not have been as nearly pure VIII as they supposed.

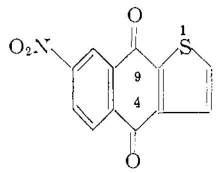
Since both VI and VII are recovered unchanged from solutions in sulfuric acid under mild conditions but both VI and VII are converted to about the same mixture of VIII and IX under more drastic conditions, the rearrangement of VI to VII and *vice versa* occurs only under conditions drastic enough to effect ring closure to quinone.



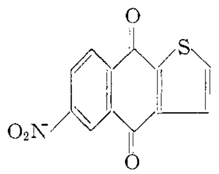
VI, m.p. 180°



VII, m.p. 193°



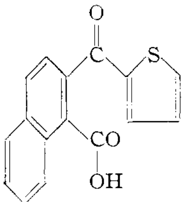
VIII



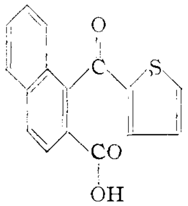
IX

In this case the explanation for the difference between our results and those of previous workers[6,9] is not as obvious as in the case of III and IV. However, we show that pure VI melts at 179–180° whereas melting points of 170–171° and 147° were reported for VI.[6,9]

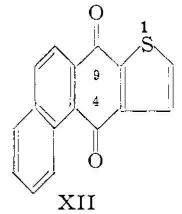
We next investigated the behavior of 2-(2-thenoyl)-1-naphthoic acid (X) and 1-(2-thenoyl)-2-naphthoic acid (XI) in sulfuric acid. Sandin and Fieser[13] reported that either X or XI yielded the same mixture of 5,6-benz-4,9-thiophanthraquinone (XII) and 7,8-benz-4,9-thiophanthraquinone (XIII), on treatment with phosphorus pentoxide in nitrobenzene at 165°. We have checked this finding and have determined that the mixture consists of about 60% of XII and 40% of XIII. In addition we found that on heating in sulfuric acid at 60° for one hour, XI is converted into X in 90% yield whereas on heating XI in polyphosphoric acid at 60° for two hours, XI is recovered unchanged.



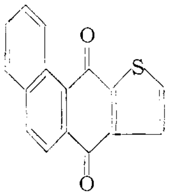
X



XI



XII



XIII

Pure samples of XII and XIII were prepared from X and XI, respectively, by reduction to the corresponding thenylnaphthoic acids, cyclization to acetoxybenzthiophanthrene derivatives, and oxidation to XII and XIII.

To summarize our findings with regard to the action of sulfuric acid on thenoylbenzoic acids, three types of behavior have been noted, as follows. A. One keto acid (III) may be rearranged into an isomeric acid (IV) under relatively mild conditions, and under more vigorous treatment leading to quinone formation only the quinone (V) formed directly from one acid (IV) is formed. B. Neither keto acid VI or VII may be rearranged into the other under relatively mild conditions but under quinone-forming conditions both keto acids are converted into the same mixture of quinones VIII and IX. C. One keto acid (XI) may be rearranged into an isomeric acid (X) under relatively mild conditions but under quinone-forming conditions, a mixture of quinones XII and XIII is formed. We believe this behavior may be described in terms of the reaction scheme

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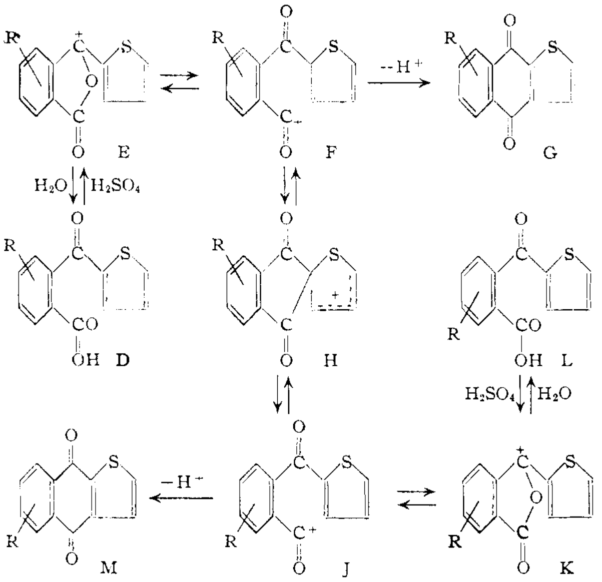
(12) Schroeder and Weinmayr, ref. 9, p. 4361, mention the loss of acid on sulfuric acid treatment and also show that 95.5% sulfuric acid at 70° for 30 min. does not isomerize III to IV.

(13) R. B. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940).



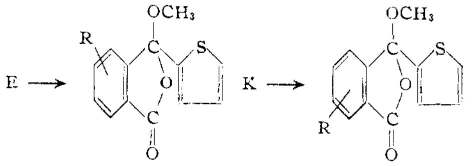
In the formulas E-M, R is any group *ortho* or *meta* (or both as in a ring fusion, *e.g.*, naphthalene ring, compounds X and XI) to the nearer carbonyl group. Also, instead of the thiophene ring, a substituted phenyl ring (or other unsymmetrical substituent) may be involved in the more general case.

The key intermediate in this scheme is H, essentially the type of substance originally proposed by Hayashi[4] to account for the rearrangement and recently reaffirmed by Sandin.[7] We have merely elaborated the scheme in more detail in order to clarify the behavior of different keto acids and to aid in predicting behavior of other keto acids of this type. The information supporting the various steps is summarized below.

The conversion of starting keto acid D to the cyclic carbonium ion E in 100% sulfuric acid has been established and discussed for the case of *o*-benzoylbenzoic acid.[14] At moderate temperatures the cyclic form E is predominant but at higher temperatures the equilibrium favors the open chain form F which may either cyclize to the quinone G or may cyclize to the intermediate H. This key intermediate will be in equilibrium with open chain ions F and J. Structural features are important in determining the position of this equilibrium as will be discussed below. The ion J may either cyclize to the quinone M or to the cyclic ion K, which, on quenching with water, yields keto acid L isomeric with starting acid D. The equilibrium J $\rightleftarrows$ K is affected by temperature much as is the equilibrium E $\rightleftarrows$ F, lower temperatures favoring the cyclic ions E and K.

In those cases where R is adjacent to a carbonyl group there appears to be a greater tendency to form the more sterically hindered ion J than the isomeric ion F.[15] A similar selectivity was first shown in the preferential reaction of the 1-carboxyl group in 2,6-dimethylterephthalic acid in the Schmidt reaction.[16] The tendency of the hindered carboxyl group to react preferentially in the Schmidt reaction has been amply demonstrated in an extensive study of 3-substituted-phthalic acids.[17] The results with these two types[16,17] show that kinetically speaking there is a preference for reaction at the more hindered of two carboxyl groups. In the present case the greater tendency to form the more hindered oxo-carbonium ion under equilibrium conditions is demonstrated.

Although no freezing point depression measurements in sulfuric acid were carried out, we obtained evidence about the type of carbonium ions present by pouring sulfuric acid solutions of the keto acids into methanol and determining the type of ester formed.[14,18] In all cases mainly pseudo-ester was obtained. The formation of pseudo-ester is a clear indication that a cyclic carbonium ion of type E or K was present.[14] The concentration of pseudo-ester was determined by a spectral method (infrared). Of the six acids, III, IV, VI, VII, X and XI, tested this way III gave by far the smallest amount of ester (10%), IV, VI and VII gave intermediate amounts (47–56%), and X and XI were almost completely esterified (88–94%). The amounts of ester formed (mostly pseudo in each case) give a fairly accurate estimate of the amount of cyclic carbonium ion, E or K, present in the sulfuric acid solutions.



Normal esters were formed by treatment of the acids with diazomethane and pseudo-esters were made by treating methanol containing dissolved urea with the acid chlorides, which in each case were cyclic acid chlorides as shown by single carbonyl absorption bands at 5.6 to 5.7 μ. It is interesting that, of the substances added to prevent the catalytic conversion of pseudo to normal ester by the hydrogen chloride present after reaction of the acid chloride with methanol, urea proved more generally effective than substances such as pyridine, 2,4,6-collidine, sodium acetate and dipotassium hydrogen phosphate.

Experimental[19]

3-Nitro-2-(2-thenoyl)-benzoic Acid (III) and 6-Nitro-2-(2-thenoyl)-benzoic Acid (IV).—Condensation of 2-thienylmagnesium bromide with 3-nitrophthalic anhydride was effected essentially as described.[20] However, on several recrystallizations of the acidic fraction, m.p. near 170°,

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[14] M. S. Newman, This Journal, **64**, 2324 (1942); see also M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

[15] Sandin, *et al.*, ref. 7, noted the same factor yet were reluctant to ascribe a general tendency because of the conflicting facts reported.[6] However, the work now reported removes this exception.

[16] M. S. Newman and H. L. Gildenhorn, This Journal, **70**, 317 (1948).

[17] Unpublished work of Dr. H. L. Shechter, *et al.*; see Ph.D. theses (Ohio State University) of H. Barkemeyer and T. Moritsugu who have studied the acids in which the 3-substituent was methyl, ethyl, fluoro, chloro, iodo, nitro, hydroxy, and methoxy. Other substituted acids were studied also.

[18] M. S. Newman, This Journal, **63**, 2431 (1941).

[19] All melting points are corrected, unless otherwise noted, and were taken in a Hershberg melting point apparatus with short stem total immersion thermometers calibrated by the U. S. Bureau of Standards. Melting points with the notation "block" were taken on a Lindstrom block, F. Lindstrom, *Chem. Fabrik*, **7**, 270 (1934).

[20] V. Weinmayr, This Journal, **74**, 4353 (1952).

from aqueous alcohol there was isolated pure IV, m.p. 191.0–192.0°.

Anal. Calcd. for $C_{12}H_7NO_5S$: C, 52.0; H, 2.6. Found:[21] C, 52.0; H, 2.6.

The structures of III and IV were established by decarboxylation to 2-nitrophenyl 2-thienyl ketone, m.p. 99.0–99.5°, and 3-nitrophenyl 2-thienyl ketone, m.p. 124.5–125.5°, respectively. Identity was established by mixed m.p. determinations and by comparison of X-ray powder photographs.[22,23]

Behavior of III and IV in Acidic Media.—When a solution of 1 g. of III, m.p. 215°, in 10 ml. of 100% sulfuric acid was heated at 70° for 30 minutes and then poured on ice the only water-insoluble acid isolated was IV, m.p. 190.5–192.0°, in 54% yield after one crystallization with little loss from aqueous alcohol. When the heating period was 2 minutes at 135°, a 34% yield of IV was obtained together with a 27% yield of 5-nitrothiophanthraquinone (V), m.p. 233.0–234.5°. On heating a solution of 1 g. of III in 10 ml. of polyphosphoric acid at 140° for 2 minutes, a 63% yield of unchanged III was obtained together with 14% of V. The same quinone was obtained in poor yield in one experiment in which the acid chloride of III, prepared with phosphorus pentachloride, was treated with aluminum chloride in nitrobenzene at 0° and heated to 120° for 9 hours. Compound III was recovered unchanged after treatment for one day with refluxing trifluoroacetic anhydride or after heating for 5 hours with methanesulfonic acid at 100°.

When a solution of IV in 100% sulfuric acid was held at 60° for one hour no V was obtained and the acid recovered was pure IV. A similar solution, held at 140–150° for one minute after rapid heating to this temperature, afforded V (40% yield, somewhat discolored). The acid chloride of IV, made and treated for 3 hours in the same way as the acid chloride of III, afforded a small yield of impure V.

The identity of V was established by reduction to the corresponding aminoquinone[9] and conversion to 5-chlorothiophanthraquinone,[9] shown to be identical to an authentic sample.[24]

4-Nitro-2-(2-thenoyl)-benzoic Acid (VI) and 5-Nitro-2-(2-thenoyl)-benzoic Acid (VII).—Condensation of 2-thienylmagnesium bromide with 4-nitrophthalic anhydride and separation of crude acids by successive neutralization with acetic and hydrochloric acids[6,20] yielded crude VI and VII in 52 and 26% yields, respectively. However, in order to obtain pure VI and VII, several recrystallizations from aqueous alcohol were required with considerable loss of product. Pure VI melts at 179.0–180.0° and pure VII at 192.5–193.5°.

Anal. Calcd. for $C_{12}H_7NO_5S$: C, 52.0; H, 2.6. Found (for VI): C, 52.1; H, 2.7.

The structures of VI and VII were established by decarboxylation to 3-nitrophenyl 2-thienyl ketone, m.p. 124–125°, and 4-nitrophenyl 2-thienyl ketone, m.p. 174–175°, which were compared to authentic samples.[22]

Behavior of VI and VII in Acidic Media.—When solutions of VI and of VII in 100% sulfuric acid were heated in the range 60–80° for one to three hours, almost pure VI and VII were recovered from the respective solutions. At higher temperatures a mixture of 6-nitro- and 7-nitrothiophanthraquinones, IX and VIII, was obtained, but, in each case where ketoacid was recoverable, it proved to be almost pure starting acid. The best yield (65%) of this quinone mixture was obtained when VII was heated at 170° for 5 minutes in polyphosphoric acid.

Composition of Mixture of Quinones VIII and IX.—Despite many attempts we were unable to devise a suitable analytical procedure to establish the composition of the above described quinone mixture. Hence the mixture was converted *via* the aminoquinones to the corresponding chloroquinones,[9] pure samples of which were supplied by Dr. Weinmayr.[24] The X-ray powder photograph of the chloroquinone mixture obtained did not compare well with those obtained from either 6-chlorothiophanthraquinone, m.p. 214°, or 7-chlorothiophanthraquinone, m.p. 190°. However, a mixture of about 50% of each afforded a photograph which compared very well with that obtained from the chloroquinone mixture resulting from conversion of the nitroquinone mixture. We assume, therefore, that the original nitroquinone mixture was composed of about equal parts of the two quinones. At various stages of this work painstaking efforts were made to separate pure quinones from the mixture present but because of almost identical physical properties we were unable to do this. It should be emphasized that we always used the *entire* quinone mixture formed in any reaction for further work. No recrystallization was done because of the change in composition this would cause.

2-(2-Thenoyl)-1-naphthoic Acid (X) and 1-(2-Thenoyl)-2-naphthoic Acid (XI).—These acids were prepared from 2-thienylmagnesium bromide and 1,2-naphthalic anhydride essentially as described for 2-thienylmagnesium iodide.[13] There was obtained a 34% yield of X, m.p. 156.5–157.5°, and a 16% yield of XI, m.p. 219.0–220.3°.

Behavior of X and XI in Acidic Media.—When solutions of X in 100% sulfuric acid were heated at 80° for 5 to 15 hours and poured on ice only X was recovered, water-soluble material being formed in larger amount the longer the heating period. After heating X in sulfuric acid or polyphosphoric acid at 160° for 3 minutes only X was recovered. After heating X in polyphosphoric acid at 120° for 90 minutes, 31% of a mixture of 5,6-benz-4,9-thiophanthraquinone (XII) and 7,8-benz-4,9-thiophanthraquinone (XIII), was formed and 35% of X was recovered. Thus, under conditions drastic enough to cause quinone formation there is a tendency for X to rearrange into XI. In contrast, on heating XI in sulfuric acid at 60° for 1 hour, X was obtained in 90% yield. Polyphosphoric acid is not a suitable medium in which to effect rearrangement as on heating XI at 60° for 2 hours or at 140° for 90 minutes mainly XI was recovered. In the latter experiment 37% of the mixture of quinones XII and XIII, described below, was produced.

When either X or XI or a mixture of the two was treated with sulfuric or polyphosphoric acid under quinone-forming conditions a mixture of XII and XIII was formed as previously found.[13] This mixture proved exceedingly difficult to analyze by chromatography or fractional crystallization. Accordingly pure samples of XII and XIII were prepared as described below.

5,6-Benz-4,9-thiophanthraquinone (XII) and of 7,8-Benz-4,9-thiophanthraquinone (XIII).—A mixture of 2.39 g. of X, 15 g. of potassium hydroxide, 12 g. of zinc dust and 250 ml. of water was refluxed for 15 hours, during which time the color changed from red to green to almost colorless. The cream-colored 2-(2-thenyl)-1-naphthoic acid obtained on acidification weighed 1.64 g. (73%) and melted at 88–90°. Without further purification a mixture of 0.36 g. of this acid, 3 ml. of acetic acid, 3 ml. of acetic anhydride and 0.01 g. of freshly fused zinc chloride was refluxed for 30 minutes and diluted with water. The brown oil which separated yielded 0.30 g. (76%) of 4-acetoxy-5,6-benzthiophanthrene, m.p. 152–154° on trituration with alcohol. A mixture of 0.12 g. of this acetate, 10 ml. of acetic acid and 0.12 g. of chromic oxide was refluxed for 5 minutes, 1 ml. of concentrated hydrochloric acid was added, and the mixture refluxed for 10 minutes. The reaction product was vatted twice to yield 0.05 g. (46%) of crude XII, which on crystallization from alcohol (Darco) yielded pure XII, m.p. 164.0–165.5°, with little loss.

In a similar way XI was reduced to 1-(2-thenyl)-2-naphthoic acid, m.p. 180–182°, in 68% yield. This crude acid was cyclized to 4-acetoxy-7,8-benzthiophanthrene, m.p. 176.5–178.5°, in 71% yield, and this acetate oxidized to XIII, m.p. 199–201°, in 30% yield. Recrystallization

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[21] All microanalyses by the Galbraith Laboratories, Knoxville, Tenn.

[22] X-Ray powder diffraction patterns were taken with a camera of 360 mm. circumference using Cu radiation and exposure times of 2.5–3.0 hours. In all cases in this work where identity was established by mixed m.p. determinations, it was confirmed by X-ray analysis.

[23] Decarboxylation and identification of ketones were carried out by both the Fordham group (ref. 6) and by Weinmayr (ref. 20) on the acid, m.p. about 170°, presumably pure IV, isolated by these workers, which we have shown to be impure. Their results can be readily understood when the fact that 3-nitrophenyl 2-thienyl ketone has a higher melting point (125°) than 2-nitrophenyl 2-thienyl ketone (100°) is noted. We believe that the acid, m.p. near 170°, consisted of a mixture of III and IV. We do not believe that our acid IV, m.p. 191–192°, is a polymorphic form of the 170° acid because of the large losses which occurred on recrystallization until the higher m.p. was attained.

[24] We are indebted to Dr. V. Weinmayr for supplying samples of V and other compounds used in this work.

several times from alcohol (Darco) afforded pure XIII, m.p. 205.2–206.2°.

Anal. Calcd. for $C_{16}H_8O_2S$: C, 72.6; H, 3.0. Found: C, 72.6; H, 2.9.

The mixture of quinones XII and XIII formed by cyclization of X and XI was analyzed by infrared spectroscopy in carbon disulfide solution using bands for XII at 7.55, 7.95, 10.95 and 12.2 μ and bands for XIII at 7.7 and 10.5 μ, and by comparison of melting range with a melting point curve diagram. Analysis by each method indicated that the same mixture of quinones formed on cyclization of X or XI consisted of about 60 ± 5% of XII and 40 ± 5% XIII.

Preparation of Normal and Pseudo Methyl Esters.—All normal methyl esters were prepared by treatment of ethereal solutions with diazomethane. The esters so obtained in almost quantitative yield were recrystallized from methanol to constant melting points. The pseudo-esters were prepared[25] by shaking about 1 g. of acid chloride with 40 ml. of methanol saturated with urea at room temperature for 4 hours. The reaction mixture was then poured into water and the ester extracted with ether–benzene. These extracts were immediately washed with 10% potassium carbonate solution and dried by passing over magnesium sulfate. The solvents were removed under vacuum and the crystalline residues recrystallized from pure methanol in flasks which had been steamed out for several minutes to remove possible traces of absorbed acid. The acid chlorides were prepared by heating the pure acids and an excess of pure thionyl chloride for 3 hours at reflux. The reagent was removed under reduced pressure and the acid chlorides were recrystallized from benzene–petroleum ether, b.p. 35–50°. In each case the infrared spectrum had a strong band between 5.6 and 5.7 μ which indicated that all of the acid chlorides had the pseudo (cyclic) structure. The acid chlorides were sensitive compounds and proved difficult to crystallize. The melting points are listed (but none was analyzed): III, 127.5–129.5°; IV, 117–119°; VI, 130.5–133.5°; VII, 129–130°; X, 114.5–116.5°; and XI, 147–150°. The melting points of normal and pseudo esters of III, IV, VI, VII, X and XI are listed in Table I.

Table I

Normal and Pseudo Methyl Esters

Acid	Ester	M.p., °C.	Analyses, found,[21] %[a] C	H	S
III	*n*	130.5–131.5	53.4	2.8	
	ψ	143.5–144.5	53.5	3.1	11.1
IV	*n*	118.0–119.0	53.6	3.2	
	ψ	96.0– 96.5	53.7	3.4	11.2
VI	*n*	134.7–135.5	53.5	3.3	
	ψ	91.2– 92.0	53.5	2.9	10.9
VII	*n*	160.0–161.0	53.7	3.4	
	ψ	87.0– 88.5	53.3	2.9	
			Found[21b]		
X	*n*	139.8–140.4	68.8	4.2	
	ψ	113.6–114.2	69.2	3.9	
XI	*n*	138.8–139.8	69.0	4.0	
	ψ	117.5–118.6	68.8	4.3	

[a] Calcd.: C, 53.6; H, 3.2; S, 11.0. [b] Calcd.: C, 68.9; H, 4.1.

Table II

Esterification in 100% Sulfuric Acid[14,18]

Acid	Acid recovd., %	Ester, % Formed	Ester, % Normal	Pseudo
III	77	10	4	96
IV	42	47.5	12	88
VI	30	65.5	5.5	94.5
VII	36	56	5	95
X	Trace	94	6	94
XI	1	88	6	94

Esterification with 100% Sulfuric Acid.—In each experiment 0.50 g. of finely ground keto acid was dissolved in 5 ml. of 100% sulfuric acid at room temperature. Shortly after the last solid had dissolved the solution, usually red, was stirred into 50 ml. of cold methanol. This solution was then poured into 150 ml. of water and the products were extracted thoroughly with ether. These extracts were well extracted with 10% potassium carbonate to remove acid. The ether solution was then dried by filtration through magnesium sulfate and solvent removed by evaporation in an apparatus arranged so that the residue could be collected quantitatively by sublimation under reduced pressure onto a cold finger. The esters thus obtained were analyzed by taking the infrared spectra of the mixtures in chloroform solutions of known concentration and matching the absorption of the ketone carbonyl (near 6.0 μ) with solutions of known concentration of pure normal ester.

The results of these esterifications are listed in Table II. It is likely that pure pseudo-ester formed initially in every case as blank experiments, in which 100% sulfuric acid was added to solutions of pure pseudo-ester dissolved in methanol, showed that about 7–10% of pseudo-ester was isomerized into normal ester in times which approximated the times required to work up the experiments cited above.

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[25] Compare M. S. Newman and C. D. McCleary, This Journal, **63**, 1537 (1941).

[Contribution from the William H. Nichols Laboratory, New York University]

Alkylation and Cyclization of Benzoylacetanilides[1]

By A. Langley Searles[2a] and Daniel Ressler[2b]

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Benzoylacetanilide and *p*-nitrobenzoylacetanilide have been mono- and di-α-alkylated with alkyl halides, using ethanolic sodium ethoxide or sodium hydride in dimethylformamide. O-Alkylation often accompanied C-alkylation, and the enol ethers thus produced occasionally comprised the chief products of the reaction. All types of alkylated products were convertible into 3-alkyl-4-arylcarbostyrils by the action of sulfuric acid; in the case of the dialkylated compounds this reaction involved elimination of the α-alkyl group capable of forming the more stable carbonium ion. Electronic factors were shown to play a more important role than steric factors in the cyclization process.

It has been reported that the action of acidic reagents upon certain compounds containing a $-NHCOCR_2CO-$ moiety may bring about their dealkylation.[3-6] For two of these reactions, mechanisms have been proposed which correlate

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[3] D. Heyl and A. C. Cope, This Journal, **65**, 669 (1943).

[4] R. M. Warren, Ph.D. thesis, New York University, 1951, p. 19.

[5] E. W. Maynert and E. Washburn, This Journal, **75**, 700 (1953).

[6] A. L. Searles and R. J. Kelly, *ibid.*, **78**, 2242 (1956).