

3. Sulfuryl chloride acted principally as a chlorinating agent.
4. Some new relations were determined in the dimethyl series.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

CONDENSATIONS AND RING CLOSURES IN THE NAPHTHALENE SERIES. III.¹ *PERI-SUCCINOYLACENAPHTHENE*

BY LOUIS F. FIESER AND (IN PART) MARY A. PETERS

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Having found that the condensation of β -naphthol with phthalic anhydride leads to the production of a compound of an unusual structural type,^{1a} it has become a matter of interest to study the reaction of various other naphthalene derivatives with this and other anhydrides. It has been our immediate concern to investigate more fully certain condensations which fall within the field specified, but which have been described only in the patent literature. These condensations are between succinic or maleic anhydride and various substitution products of naphthalene. In a series of patents originating with the I. G. Farbenindustrie,² it is claimed that cyclic compounds of novel structure may be obtained either by heating the components in molten sodium aluminum chloride or by applying this method of condensation to the intermediate products resulting from the Friedel and Crafts reaction of the anhydride with the hydrocarbon.

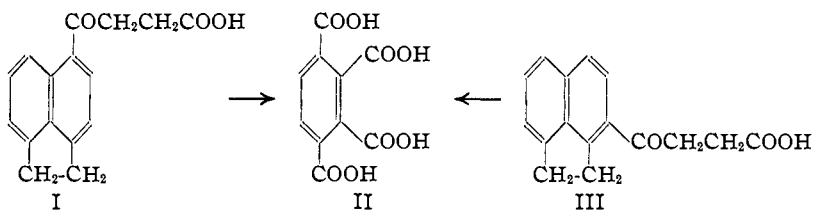
After some trial of these reactions it was decided that the case most favorable for detailed study was that of the condensation of succinic anhydride with acenaphthene. As specified in the patents, these components interact smoothly at 0° in nitrobenzene solution in the presence of aluminum chloride.³ The keto acid melting at 208° is not, however, the sole reaction product, but is accompanied by an isomer melting at 181°. The separation of the isomers is easily accomplished and it was further found that the relative proportions of the two acids is somewhat dependent upon the reaction temperature. Thus the yields at 0° were 78 and 15% for the higher and the lower melting isomers, respectively, while at -15° the yields were 87 and 5%. The structures were established by oxidation. The higher melting acid is β -(3-acenaphthoyl)-propionic acid, I, for it yields 1,4,5-naphthalenetetracarboxylic acid on controlled permanganate oxidation. No acid of the naphthalene series could be obtained from the

¹ (a) First paper, Fieser, *THIS JOURNAL*, **53**, 3546 (1931); (b) second paper, Fieser and Peters, *THIS JOURNAL*, **54**, 3742 (1932).

² (a) I. G. Farbenindustrie, French Patent 636,065 (1928); (b) Swiss Patent 131,959 (1929); (c) H. Gruene, U. S. Patent 1,759,111 (1930).

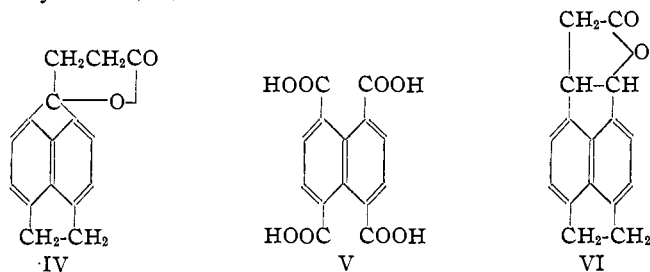
³ The reaction is also described by F. Mayer, German Patent 376,635 (1923).

isomer melting at 181° , but on complete oxidation it was converted into a substance having the properties of mellophanic acid, II.⁴



Since, however, this acid melts at practically the same temperature as the other possible oxidation product, prehnitic acid (1,2,3,5), it was necessary to obtain an authentic sample of mellophanic acid for comparison. This was conveniently prepared by oxidizing the higher melting keto acid, I, and the two products were found to be identical. The acid melting at 181° is thus β -(1-acenaphthoyl)-propionic acid, III.

When the 3-acenaphthoylpropionic acid is heated in molten sodium aluminum chloride at 150° , it is converted, with loss of the elements of water, into an alkali-insoluble, yellow compound. A condensation of the type described in our first paper^{1a} would give a substance of the structure of IV, but this formula for the yellow compound is ruled out by the observation recorded in the patent literature,⁵ which we have confirmed, that the yellow substance is converted smoothly into 1,4,5,8-naphthalene-tetracarboxylic acid, V, on oxidation.



Presumably on the basis of this reaction, the authors of the series of patents have suggested formula VI as the structure of the condensation product. This would represent not only a novel reaction but a type of ring structure which has not yet been obtained. It would be a derivative of the unknown "aceacenaphthene" which Mayer and Kaufmann sought to prepare by closing a second five-membered ring across the remaining *peri*-positions of acenaphthene.⁶ No more successful was an attempt

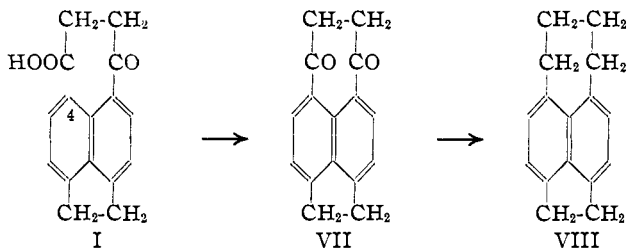
⁴ Bamford and Simonsen, *J. Chem. Soc.*, 97, 1908 (1910), proved that this is the structure of mellophanic acid, rather than of prehnitic acid, as stated in most of the current works of reference.

⁵ I. G. Farbenindustrie, Swiss Patent 134,084 (1929).

⁶ Mayer and Kaufmann, *Ber.*, 53, 289 (1920).

made in the course of the present work to effect an intramolecular Friedel and Crafts reaction with β -bromo- β -(3-acenaphthoyl)-propionic acid, a reaction which might have opened the way for a synthesis of VI. Much more significant than the failure of these attempted ring closures is the observation of Scholl that 1,4-anthrahydroquinonedicarboxylic acid forms a mono- but not a di-lactone, whereas the 1,5-acid forms a dilactone.⁷ This is a good indication of the resistance to the closing of five-membered rings across both *peri*-positions of the naphthalene nucleus.

Further study of the yellow condensation product soon showed that the properties of the compound are not consistent with the lactone formula, VI. The solubility of the compound in alcohol is indeed increased by the addition of alkali, but no salt or free acid could be obtained. It has, on the other hand, the properties of a diketone, for it yields a dioxime, and it may be reduced smoothly by the Wolff-Kishner method. These facts, together with the result of oxidation, establish the structure, indicated in formula VII, of *peri*-succinoylacenaphthene. The reduction product must have the structure of VIII. The condensation involves the splitting



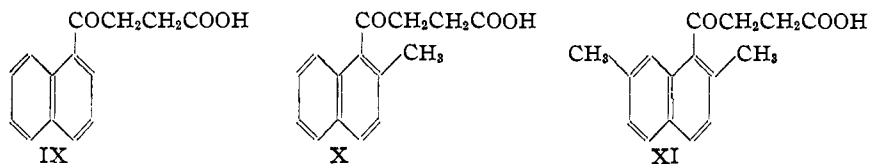
out of water between the carboxyl group of the keto acid, I, and the hydrogen atom in position 4. The surprising feature of the reaction is that it leads to the closure of a seven-membered ring. The aromatic keto acids condense readily enough under the influence of aluminum chloride, but they yield 6-ring products.^{1b}

It is of interest to inquire into the factors favoring the unusual condensation here noted. The difficulty of formation of a 7-ring, particularly where the closure of a 6- or 5-ring is also possible, is clearly indicated by the investigations of von Braun.⁸ In the case of acenaphthoylpropionic acid, the closure of a 6-ring is also possible, but it would involve substitution at a position *ortho* to an unsaturated group, and it is perhaps this factor which impedes the reaction. It is reasonable to suppose that, on the other hand, the closing of a 7-ring through a *peri* condensation is facilitated by the presence of the acenaphthene dimethylene bridge, which must activate the 4-position. This idea is to a certain extent substantiated

⁷ Scholl and Böttger, *Ber.*, **63**, 2128 (1930).

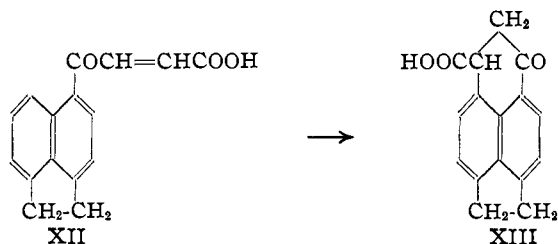
⁸ Von Braun and collaborators, *Ann.*, **468**, 259, 277 (1929); *Ber.*, **50**, 56 (1917); **59**, 1922 (1926); **60**, 1182 (1927); **61**, 956 (1928); **62**, 145 (1929).

by the observation that β -(1-naphthoyl)-propionic acid (IX), in which such activation is lacking, does not undergo condensation but is converted into the 2-isomer in the sodium aluminum chloride melt. Attempts to pursue the question further through a study of the methylated acids X



and XI were without conclusive result, for we were unable to isolate any reaction products from the resins resulting from the action of aluminum chloride on these substances. No better results were obtained with the keto acid prepared from β -naphthol and succinic anhydride.

In short, in so far as our observations extend, the formation of *peri*-succinoylacenaphthene represents a wholly unique reaction. In no other case investigated do all of the features of structure so combine to favor the closing of a 7-ring as they do in the case of β -(3-acenaphthoyl)-propionic acid. That even the corresponding acenaphthylbutyric acid reacts in a different manner will be shown in a forthcoming paper. The claim set forth in the patents that the formation of cyclic compounds of this type is a general one is thus to be discounted. It should be stated, however, that not all of the condensations claimed in the patents in question are of exactly the above type, for some of them involve the use of an unsaturated keto acid. We have made no study of this type of reaction beyond preparing and analyzing the condensation product from the unsaturated acid XII.



The substance is acidic and isomeric with the starting material, so that the reaction is evidently quite different from the one described above. It appears probable that the reaction consists in intramolecular addition to the conjugated system, and that the condensation product has the structure of XIII.

Experimental Part

1. Preparation of the Acenaphthoyl Propionic Acids.—The essential features of the general procedure given in the patent literature^{2,3} for the condensation of succinic anhydride with naphthalene and its derivatives are: the use of nitrobenzene as the

solvent, a low reaction temperature, a 10% excess of the anhydride and of aluminum chloride. In the course of our work we took occasion to change the solvent, the temperature and the molecular ratio, but the best results were always obtained by adhering to the conditions specified.

A solution of 100 g. of pure acenaphthene and 72 g. of succinic anhydride in 600 cc. of nitrobenzene was prepared in a 3-liter long-necked flask equipped with a mechanical stirrer working through a 3-way addition tube, and cooled in a large ice-bath. In the course of one hour 195 g. of aluminum chloride was added in small portions. Stirring was continued at 0° for four hours more and the deep red solution was allowed to stand for twelve hours and come to room temperature. After the cautious addition, with cooling, of 200 g. of ice and 100 cc. each of water and concentrated hydrochloric acid, the solvent was removed with a rapid stream of steam and using an efficient condensing system. After about one and one-half hours the product separated as a pasty lump which disintegrated after four to five hours of further steaming to a grayish-white powder. This material was collected, dissolved in a solution of 115 g. of sodium carbonate decahydrate in 1 liter of water, and the last traces of nitrobenzene were removed by steam distillation. One hundred grams of sodium chloride was dissolved in the hot, filtered, brown solution, which was then allowed to cool without disturbance. The sodium salt of β -(3-acenaphthoyl)-propionic acid separated as colorless, fibrous needles, while the 1-acid largely remained in solution. The solid was washed free of the dark mother liquor (A) with half-saturated sodium chloride solution and crystallized a second time from a hot, clarified solution containing 50 g. of sodium chloride. The mother liquor (B) was again saved. On acidifying a solution of the purified sodium salt the 3-acenaphthoylpropionic acid was obtained as a white powder and in very pure condition; m. p. 208°; yield, 120 g. (73%).

On acidifying the first mother liquor (A) there was obtained a product which was dark and tarry but which soon solidified on being stirred. After boiling a soda solution of the material with animal charcoal and reprecipitating it from a cold solution, a light tan product was obtained (35 g.). It was combined with the solid (8 g.) precipitated from the mother liquor (B) and esterified with methyl alcohol (300 cc.) and sulfuric acid (15 cc.). On boiling for a short time the material all went into solution and on cooling there was obtained a mass of dark crystals consisting largely of the ester of β -(1-acenaphthoyl)-propionic acid. This is considerably less soluble than the 3-ester, and it was easily obtained in pure condition by crystallization from alcohol; m. p. 126°; yield, 26.4 g. (15%). The recovery of the 3-acid from the alcoholic mother liquors is hardly profitable, but it is easily accomplished by concentrating the solutions, hydrolyzing with alkali, and purifying the 3-acid through the sodium salt, the yield being 8 g. (5%).

The total yields at 0° were thus 78% of the 3-acid and 15% of the 1-acid. At -15° these substances were obtained in yields of 87 and 5%, respectively. At room temperature there was some increase in the proportion of the 1-acid but the product was very dark and difficult to work up and the total yield was lower.

β -(3-Acenaphthoyl)-propionic acid (I) is only moderately soluble in glacial acetic acid, alcohol or xylene, but it crystallizes well from these solvents as stout needles melting at 208° with some decomposition. It decomposes somewhat on distillation at diminished pressure. The solution in concentrated sulfuric acid is red and the material is either sulfonated by this treatment or recovered unchanged. Only dark tars were obtained on attempting to prepare an acid chloride.

*Anal.*⁹ Calcd. for C₁₆H₁₄O₂: C, 75.56; H, 5.55. Found: C, 75.55; H, 5.65.

⁹ The analyses here reported were ably carried out by Mr. C. L. Bickel.

The methyl ester was prepared by heating a suspension of 100 g. of the acid in 500 cc. of methyl alcohol with 25 cc. of concentrated sulfuric acid. The material soon dissolved and the ester was deposited on cooling in good yield and in nearly pure condition. The substance is very soluble in methyl alcohol and forms plates melting at 89°.

Anal. Calcd. for $C_{17}H_{15}O_3$: C, 76.09; H, 6.01. Found: C, 76.35; H, 6.22.

The methyl ester oxime forms colorless needles, m. p. 146°, from benzene-ligroin.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05. Found: C, 72.29; H, 6.02.

β -(1-Acenaphthoyl)-propionic acid (III), obtained by hydrolyzing the ester with alcoholic alkali, crystallized from dilute alcohol as small needles melting at 181°. It is considerably more soluble than the isomer and this is also true of the sodium salt. The sulfuric acid solution is red-orange in color.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.79; H, 5.77.

The methyl ester gives long needles from alcohol or dilute acetic acid, m. p. 126°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.16; H, 5.98.

2. Oxidation of the Keto Acids.—Attempts to convert β -(3-acenaphthoyl)-propionic acid into an acenaphthenecarboxylic acid were without success. The first oxidation product isolated, using 12.7 g. of the acid and 48 g. of potassium permanganate in alkaline solution, was a yellow acid melting at 259° which has not been identified.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.85; H, 3.97. Found: C, 71.05; H, 3.76.

Oxidation of the same quantity of acid with 64 g. of potassium permanganate gave 1,4,5-naphthalenetetracarboxylic acid. At the end of the reaction the mixture was treated with sulfur dioxide, which dissolved the brown precipitate and gave a clear solution. On adding hydrochloric acid and heating, the oxidation product precipitated in the form of the anhydride (5 g.). Crystallized from dilute alcohol it melted at 274°.

Anal. Calcd. for $C_{13}H_6O_5$: C, 64.46; H, 2.50. Found: C, 64.62; H, 2.64.

It was found that the monomethyl ester of the anhydride is a convenient derivative with which to characterize the compound. It is easily prepared by esterification of the anhydride with methyl alcohol and sulfuric acid. Being sparingly soluble in the medium, it separates at once from the hot solution. It crystallizes well from glacial acetic acid as colorless needles melting at 222°.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.15. Found: C, 65.34; H, 3.34.

The 1,4,5-naphthalenetetracarboxylic acid anhydride was identified by comparison with a sample, m. p. 274°, prepared according to Graebe.¹⁰

Mellophanic acid was obtained by gradually adding 105 g. of potassium permanganate to a hot solution of 12.7 g. of the keto acid in 500 cc. of water containing 3 g. of potassium hydroxide, and heating the mixture for one hour on the steam-bath. The solution was decolorized by the addition of a little alcohol, filtered, and the precipitated manganese dioxide was extracted thoroughly with hot water. The filtrate and washings were acidified, boiled down to a volume of 500 cc. and treated with 32 g. of hydrated barium hydroxide. The precipitated barium salt was digested at the boiling point, collected, and boiled with 200 cc. of water containing 3 cc. of concentrated sulfuric acid. The solution, filtered from barium sulfate, was evaporated to a sirup, cooled and treated with 50 cc. of concentrated hydrochloric acid. This precipitated the mellophanic acid in a colorless, crystalline condition; m. p. 236°, with loss of water; yield, 3.2 g. (25%). The tetramethyl ester, conveniently prepared with diazomethane, melted at 129–130°, which corresponds with the observations recorded in the literature.

¹⁰ Graebe, *Ann.*, **327**, 77 (1903).

This method of preparing mellophanic acid has some advantages over the many methods previously recorded, for the starting material is easily prepared and the usual sealed-tube reaction is avoided.

Oxidized in exactly the same manner, β -(1-acenaphthoyl)-propionic acid likewise gave mellophanic acid, m. p. 233°, ester 129–130°.

3. *Peri-succinoylacenaphthene*.—The best results were obtained by condensing the ester rather than the free keto acid. The condensation product was also obtained directly from acenaphthene and succinic anhydride, as specified in the patent literature, but the yields were very poor.

A melt was prepared by fusing together 50 g. of sodium chloride and 250 g. of aluminum chloride. When it had cooled to the point of incipient crystallization (100°), 40 g. of β -(3-acenaphthoyl)-propionic acid methyl ester was stirred in in the course of five minutes. The bright red melt was stirred well, brought to 150° in fifteen minutes, and kept at that temperature for one-half hour, when it had become dark brown. It was stirred into ice and water, which precipitated a dull yellow, slightly tarry product (25 g.). This was boiled with glacial acetic acid and the solution was filtered from a black residue, boiled down and treated with water. The product which precipitated was dried well and distilled *in vacuo*. A considerable residue was left, but the distillate was a good yellow solid from which the pure diketone was easily obtained by crystallization; yield, 15.2 g. (43%).

Peri-succinoylacenaphthene is readily soluble in benzene or glacial acetic acid, moderately soluble in alcohol, and it crystallizes well from any of these solvents, forming long, flat, yellow needles melting at 180°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.25; H, 5.19.

In concentrated sulfuric acid it forms a yellow solution with a faint green fluorescence. Working in the absence of air, it was observed that a suspension of the diketone in alcohol could be brought into solution by the addition of alkali. No stable sodium salt is formed, however, for the diketone precipitated when a relatively small amount of water was added. The solution in alcoholic alkali turns green and then brown on exposure to the air and a black substance is formed. The diketone is not affected by boiling with acetic anhydride and sodium acetate; it is converted into a black tar by concentrated hydrochloric acid at 200°. When heated with methylmagnesium iodide at 100°, 0.2 mol. equiv. of gas was given off and the total consumption of reagent was 2.0 mol. equivalents.

The dioxime was prepared by warming a mixture of 4 g. of the diketone, 6 g. of hydroxylamine hydrochloride, and 30 cc. each of water, alcohol and 6 *N* sodium hydroxide solution until all of the solid had dissolved. The dioxime (4.4 g.) precipitated when the solution was acidified. It crystallized from glacial acetic acid as small, pale yellow needles which decompose on heating. It dissolves easily in concentrated hydrochloric acid and is easily hydrolyzed by this reagent, the diketone crystallizing from the warmed solution.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30. Found: C, 72.27; H, 5.25.

The dioxime diacetate crystallizes well from acetic anhydride as tan needles.

Anal. Calcd. for $C_{20}H_{18}O_4N_2$: C, 68.55; H, 5.18. Found: C, 68.87; H, 5.23.

Oxidation of the diketone (2.5 g.) in glacial acetic acid (50 cc.) was carried out, as specified in the patent to which reference has been made,⁵ by the addition in portions of 25 g. of sodium dichromate at 80–90°. After boiling the solution for three hours it was poured into 150 cc. of dilute sulfuric acid. The oxidation product was heated in alkaline solution with 0.5 g. of potassium permanganate and reprecipitated from the decolorized and filtered solution. It formed colorless, glistening crystals (1.6 g.).

While 1,4,5,8-naphthalenetetracarboxylic acid has no characteristic melting point, it responds to certain highly specific tests (dissolution of the dianhydride in ammonia solution, precipitation of the diimide, formation and decomposition of the yellow sodium salt of the diimide).¹¹ Our product corresponded precisely with the description given.

Peri-tetramethyleneacenaphthene (VIII).—We had no success in attempting to reduce the diketone by the Clemmensen method, but the Wolff-Kishner reaction proved satisfactory. A mixture of 1.2 g. of the material, 0.5 cc. of hydrazine hydrate and a solution of 0.9 g. of sodium in 12.5 cc. of absolute alcohol was heated at 160° for eight hours. The reaction product was rather dark colored, but it was easily purified by distillation and crystallization from ligroin. The hydrocarbon gives clusters of well-formed, colorless needles melting at 138°.

Anal. Calcd. for C₁₈H₁₆: C, 92.25; H, 7.75. Found: C, 92.27; H, 7.72.

4. **Other Keto Acids.**—As stated in the theoretical part some attempts were made to obtain ring compounds similar to that resulting from the action of aluminum chloride on β -(3-acenaphthoyl)-propionic acid by subjecting similarly constituted acids to the same treatment. Since these attempts were in every case unsuccessful, it will be sufficient here to record very briefly a description of the new compounds investigated. Their properties and analyses are recorded in the table. The condensations of succinic anhydride with β -methylnaphthalene, 2,7-dimethylnaphthalene or β -methoxynaphthalene were carried out in the manner described in the first section, but the products were not as easily purified, for their sodium salts could not be crystallized, and the yields were poorer (60–75%). The reaction of glutaric anhydride and acenaphthene gave a particularly poor result.

KETO ACIDS AND DERIVATIVES

	Carbon, %		Hydrogen, %		M. p., °C.
	Calcd.	Found	Calcd.	Found	
β -(2-Methyl-1-naphthoyl)-propionic acid ¹²	74.36	74.24	5.83	6.00	168
Methyl ester	74.97	74.89	6.30	6.51	85
β -Bromo deriv. of methyl ester	57.32	56.99	4.51	4.54	81
β -(2,7-Dimethyl-1-naphthoyl)-propionic acid	74.97	74.97	6.30	6.33	130
β -(2-Hydroxy-1-naphthoyl)-propionic acid	68.83	68.38	4.96	5.10	232
β -(2-Methoxy-1-naphthoyl)-propionic acid	69.75	69.68	5.47	5.55	152
γ -(3-Acenaphthoyl)-butyric acid	76.09	76.09	6.01	6.13	201
Methyl ester	76.56	76.46	6.43	6.39	120

The condensation of succinic anhydride with naphthalene using nitrobenzene as the solvent has been described recently by Haworth,¹³ and we can confirm his statements as to the general superiority of this method over the earlier procedures. Instead of a 50% excess of the hydrocarbon, as specified by Haworth, we used a 10% excess of the anhydride and obtained somewhat better yields: β -(1-naphthoyl)-propionic acid (172°), 36%; β -(2-naphthoyl)-propionic acid (129°), 47%. The latter acid was purified through the methyl ester, which distilled without decomposition *in vacuo* and which melted at 14–15°. We have found no advantage in changing the order of addition of the reagents.

¹¹ Bamberger and Philip, *Ann.*, **240**, 147 (1887); Freund and Fleischer, *ibid.*, **399**, 182 (1913).

¹² This acid without doubt is identical with the substance described as β -(6-methyl-2-naphthoyl)-propionic acid by Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932), in a paper published after completion of the present paper.

¹³ Haworth, *J. Chem. Soc.*, 1125 (1932).

In the patents of the I. G. Farbenindustrie³ the statements regarding the "condensation product" obtained by heating β -(1-naphthoyl)-propionic acid with sodium aluminum chloride are somewhat confused, but the claim appears to be to the effect that a carboxylic acid derivative of a cyclic compound is produced, and the melting point is given as either 150 or 165°. The only product which we obtained from this reaction melted, after careful purification, at 172° and was identified as β -(2-naphthoyl)-propionic acid.

5. **The Condensation of an Unsaturated Keto Acid.**—According to the patent literature maleic anhydride condenses just as well with naphthalene as does succinic anhydride, but we cannot confirm this statement. No product was isolated in the reaction with naphthalene, while with acenaphthene the yield of keto acid was very poor (32%) and the working up of the material was a very tedious process. The unsaturated acid is more easily prepared from the corresponding saturated compound through the bromo derivative.

The **Methyl Ester of β -Bromo- β -(3-acenaphthoyl)-propionic acid** was prepared by adding a solution of 16 g. of bromine in chloroform to an ice-cold solution of 26.8 g. of methyl β -(3-acenaphthoyl)-propionate in 50 cc. of chloroform in the course of one-half hour. The solvent was taken off at the water pump and the oil left as a residue was taken up in ether. The product soon separated from the solution in the form of an amorphous paste which was then crystallized from benzene-ligroin; yield, 25 g. (77%). The bromo ester forms a crust of thick, yellow prisms melting at 113°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 58.79; H, 4.36. Found: C, 58.72; H, 4.67.

Attempts to effect an intramolecular ring closure with this bromo ester were unsuccessful. Heated in carbon bisulfide solution with aluminum chloride, the substance formed a deep red addition product but was recovered unchanged. It was completely decomposed by molten sodium aluminum chloride or by heat.

β -(3-Acenaphthoyl)-acrylic Acid (XII).—A solution of 10 g. of the bromo ester and 3 g. of fused sodium acetate in 30 cc. of glacial acetic acid was heated for one hour on the steam-bath and poured into water. This precipitated a yellow oil which soon solidified and which was then crystallized from methyl alcohol. The methyl ester thus obtained (7 g.) formed yellow plates melting at 113° when completely pure.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.42; H, 5.33.

The free acid itself was obtained in poor yield by condensing acenaphthene with maleic anhydride, and the ester was compared with the above products and found to be the same. The acid forms small, yellow crystals melting at 165°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.05; H, 4.97.

Condensation Product (XIII?).—The unsaturated ester was heated in a sodium aluminum chloride melt at 140° for one-half hour and the dark brown solution was poured into water. The dark, somewhat tarry product was dissolved in soda solution and precipitated, then crystallized from alcohol. It forms canary-yellow needles melting at 214° with vigorous effervescence. The solution in concentrated sulfuric acid is yellow, with a beautiful green fluorescence.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.02; H, 4.75.

The yield of condensation product was only about 5% of the theoretical amount. The crude product is difficult to purify, and in several experiments the material was completely destroyed.

6. **Anthracene and Succinic Anhydride.**—In the hope of trying to effect a ring closure with a suitable keto acid of the anthracene series, the reaction between this hydrocarbon and succinic anhydride in nitrobenzene solution was investigated. Mayer

states in a patent³ that the sole product is an acid melting at 160°, but we obtained a complicated mixture of substances from which only one acid, m. p. 228°, was isolated. It is easily separated as the sparingly soluble sodium salt, but the yield is only 10% of the theoretical amount. The acid group was found to be in the β -position, for the substance on oxidation yielded first an anthraquinone keto acid and then β -anthraquinonecarboxylic acid, which was identified as the methyl ester, m. p. 168°, by comparison with an authentic sample. The acid is thus of no interest in connection with the present study of *peri* condensations. The properties of the acid and its derivatives may be recorded briefly.

β -(2-Anthroyl)-propionic acid: long, yellow needles, m. p. 228°. *Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.29; H, 4.88.

The methyl ester formed pale yellow blades, m. p. 148°. *Anal.* Calcd. for $C_{19}H_{16}O_3$: C, 78.05; H, 5.52. Found: C, 77.90; H, 5.51.

β -(2-Anthraquinonyl)-propionic acid: yellow needles, m. p. 207°. *Anal.* Calcd. for $C_{18}H_{12}O_5$: C, 70.11; H, 3.92. Found: C, 69.58; H, 3.95.

γ -(2-Anthryl)-butyric acid: greenish-yellow plates, m. p. 197°. *Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.11. Found: C, 81.56; H, 6.08.

Summary

When β -(3-acenaphthoyl)-propionic acid (I) is heated in molten sodium aluminum chloride, a rather remarkable intramolecular condensation takes place. A seven-membered ring is closed across the *peri* positions of acenaphthene with the formation of *peri*-succinoylacenaphthene (VII). The reaction is far from being a general one, for none of the other keto acids investigated gave similar results.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WYOMING]

SOME NEW ESTERS OF ALPHA-HEXABROMOSTEARIC ACID¹

BY KENNETH E. STANFIELD AND ERNEST R. SCHIERZ

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Introduction.—The solid α -hexabromostearic acid, $C_{17}H_{29}Br_6COOH$, (often called α -linolenic acid hexabromide), in contrast to its parent acid, the unsaturated linolenic acid, $C_{17}H_{29}COOH$, which forms only liquid esters, has the property of forming solid salts and esters.² As pure linolenic acid is obtained by the debromination of the solid α -hexabromostearic acid, it seems possible that the solid esters of the latter acid might also be debrominated to yield linolenic acid or its esters. As a related phase of this prob-

¹ Based upon a thesis by Kenneth E. Stanfield submitted to the Department of Chemistry, and the Committee on Graduate Work of the University of Wyoming, in partial fulfillment of the requirement for the Degree of Master of Arts (1931).

² (a) Erdmann and Bedford, *Ber.*, **42**, 1330 (1909); (b) Samuel Coffey, *J. Chem. Soc.*, **119**, 1412 (1921); (c) Imperial and West, *Philippine J. Sci.*, **31**, 441 (1926); (d) Almoradie and West, *ibid.*, **33**, 257 (1927); (e) Vincente and West, *ibid.*, **36**, 73 (1928).