Tetra-n-butyloxamidine from sym-bis(2-methoxyethyl)oxaldiimidate and butylamine. A mixture of 3.0 g. (0.11 mole) of *sym*-bis(2-methoxyethyl)oxaldiimidate dihydrochloride and 12.0 g. (1.64 moles) of *n*-butylamine was refluxed for 3 hr. The solution was poured into 300 ml. of water and the precipitate filtered by suction. Recrystallization from petroleum ether gave white crystals melting at 85–86°. Admixture with tetra-*n*-butyloxamidine[15] resulted in a melting point of 85–86°.

sym-Di-n-butyloxamidine dihydrochloride from sym-bis-(2-hydroxypropyl)oxaldiimidate dihydrochloride and butylamine. A solution of 1.0 g. (0.004 mole) of *sym*-bis(2-hydroxypropyl)oxaldiimidate dihydrochloride dissolved in 0.6 g. (0.008 mole) of *n*-butylamine was mixed with 25 ml. of dimethyl Cellosolve and refluxed for 5 min. Petroleum ether was added to the cooled mixture until it turned turbid. An oil separated, which was frozen solid by the use of Dry Ice. The solvent was then decanted and the residue dissolved in ethanol. Dry hydrogen chloride was passed into the solution and the white precipitate filtered by suction. It melted at 270°. When mixed with pure di-*n*-butyloxamidine dihydrochloride,[11] it melted at 268–269°.

sym-Diphenyloxamidine from sym-bis(2-hydroxyethyl)oxaldiimidate and aniline. By dissolving the diimidate dihydrochloride in aniline and allowing the solution to stand at room temperature for several hours, a 32% yield of *sym*-diphenyloxamidine[16] was obtained. Recrystallized from benzene, the product melted at 208–212°; mixed with diphenyloxamidine at 210–214°.

Bis(Δ^2-2-imidazolinyl) from sym-bis(2-hydroxyethyl)oxaldiimidate and ethylenediamine. Two grams of the diimidate was dissolved in 15 ml. of 95% ethylenediamine solution and heated in a hot water bath for 5 min. On cooling, a white solid precipitated. The mixture was diluted with water and the solid filtered off and recrystallized from alcohol. Melting point (sealed tube) 289–292°; mixed with bis-(Δ^2-2-imidazolinyl),[4] 286–290°.

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(16) A. W. Hofmann, *Ann.*, **66**, 130 (1848).

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

Acenaphthene Chemistry. IV.[1] The Aluminum Chloride Catalyzed Diacylation of Acenaphthene

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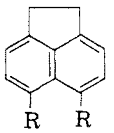
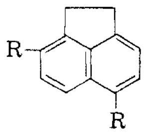
3,6-Dibenzoylacenaphthene is formed by the direct acylation of acenaphthene in the Friedel-Crafts reaction. It was converted into the dioxime which was rearranged to the dibenzamide and then hydrolyzed to 3,6-diaminoacenaphthene. The diacetylacenaphthene formed by direct acetylation was shown to be 3,6-isomer and not the 5,6-diacetyl compound as reported.

The literature gives numerous examples of electrophilic substitution in the acenaphthene nucleus. Reactions such as nitration, sulfonation, halogenation, and acylation with aluminum chloride give predominately 5-substituted acenaphthenes.[3] It has been established that monoacetylation will produce a small amount of the 3-isomer.[4,5] If these mono substituted derivatives are subjected to further electrophilic attack the entering group shows a strong preference for the 6 position.[6–9] Disubstituted derivatives have been prepared by the Friedel-Crafts reaction. Thus Dziewonski and Spirer[10] prepared a diacetyl derivative m.p. 149° which they described as the 5,6-isomer I since the dioxime is reported to rearrange to the diacetamide II which was hydrolyzed to the known 5,6-diaminoacenaphthene III. Similar reactions were used to characterize a dipropionyl derivative.[11] The formation of 4,7-di-*t*-butylacenaphthene by means of the Friedel-Crafts reaction has been definitely established.[3]



I. R = $COCH_3$
II. R = $NHCOCH_3$
III. R = NH_2
IV. R = COC_6H_5
V. R = $NHCOC_6H_5$
VI. R = COOH



VII. R = NH_2
VIII. R = $NHCOC_6H_5$
IX. R = COC_6H_5
X. R = $COCH_3$
XI. R = $NHCOCH_3$
XII. R = COOH

In our work the 5,6-dibenzoylacenaphthene (IV) was desired. The patent literature[12] describes a dibenzoylacenaphthene, m.p. 143°, and a diacetyl

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(1) For paper III see H. J. Richter and B. C. Weberg, *J. Am. Chem. Soc.*, **80**, 6446 (1958). The support of this work by an Ohio Oil Co. Fellowship and a grant from the National Institute of Health (Cy-2997-Cy) is respectfully acknowledged.

(2) A portion of the dissertation submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree.

(3) H. E. Nurnsten and A. T. Peters, *J. Chem. Soc.*, 729 1950.

(4) D. Nightingale, H. E. Ungnade, and H. E. French, *J. Am. Chem. Soc.*, **67**, 1262 (1945).

(5) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **61**, 1272 (1939).

(6) F. Sachs and G. Mosebach, *Ber.*, **43**, 2473 (1910); **44**, 2852(1911).

(7) C. Graebe, *Ann.*, **327**, 77 (1903).

(8) H. J. Richter, *J. Org. Chem.*, **21**, 619 (1956).

(9) K. Dziewonski and M. Rychlik, *Bull. intern. acad. polon. sci.*, **A**, 179 (1925).

(10) K. Dziewonski and J. Spirer, *Bull. intern. acad. polon. sci.*, **A**, 232 (1931).

(11) K. Dziewonski and J. Moszew, *Bull. intern. acad. polon. sci.*, **A**, 242 (1931).

(12) O. Wulff, R. Sedhmayr, and W. Eckert, U. S. Patent **1,747,535** (1930) British Patents **291,347** (1929) and **279,506** (1928).

derivative, m.p. 146°, but no structures are assigned. A dibenzoylacenaphthene, m.p. 149–150°, was obtained in 33% yield by the acylation of acenaphthene with two equivalents of benzoyl chloride with aluminum chloride as the catalyst. This product was converted into the dioxime and rearranged. A comparison of this product with the dibenzamide V prepared from the known 5,6-diaminoacenaphthene (III) showed them to be different. The possibility that the reaction may have stopped after the rearrangement of only one of the oxime groups because of precipitation of the product was excluded since no further rearrangement occurred when it was dissolved in much solvent and again subjected to rearranging conditions.

Since Dziewonski and Spirer prepared and supposedly proved the structure of 5,6-diacetylacenaphthene, under the conditions of the haloform reaction this compound should form 5,6-acenaphthenedicarboxylic acid (VI). A diacetyl compound, m.p. 148–149°, was obtained in 19% yield by acylation in carbon disulfide and converted into a diacid in excellent yield. This acid did not melt below 340°. Freund and Fleischer[13] reported a m.p. of 293–294°, for the anhydride formed at this temperature. This result cast serious doubt on the structure reported as 5,6-diacetylacenaphthene. It is conceivable that a substituent in the 5-position would hinder attack at the 6-position and thus favor the formation of a 3,6-isomer in diacylation. There are no reported instances of 3,6-diacylation of acenaphthene.

Hydrolysis of the product obtained from the Beckmann rearrangement of dibenzoylacenaphthene dioxime with refluxing 70% sulfuric acid yielded slightly less than one equivalent of benzoic acid. An amine was isolated from this reaction which reacted with benzoyl chloride to reform the original product. An analysis of the amine indicated an amino-benzamidoacenaphthene.

With 100% phosphoric acid as the reagent for hydrolysis,[14] 1.22 equivalents of benzoic acid was isolated. The formation of more than one equivalent of benzoic acid indicated that the rearrangement formed a dibenzamide. A diamine, m.p. 100–101° was isolated from the reaction mixture.

Following the procedure of Morgan and Harrison,[15] there was obtained a 17% yield of 3-nitroacenaphthene which on further nitration formed the 3,6-dinitro compound. This was reduced to 3,6-diaminoacenaphthene (VII) m.p. 100–101°. The 3,6-dibenzamide VIII obtained from this diamine did not depress the melting point of the product obtained by rearranging the dioxime of the dibenzoylacenaphthene obtained by direct acylation. The infrared spectra were superimposable. The dibenzoyl derivative m.p. 149–150° is thus 3,6-dibenzoylacenaphthene (IX).

In view of the above results, the work described by Dziewonski and Spirer[10] for proving the structure of diacetylacenaphthene was repeated. The diacetyl compound, m.p. 149–150° (lit.[10] 149°), was converted into the dioxime using the procedure described. This compound melted at 206–208° instead of 196° as reported. The analysis indicated a diacetylacenaphthene dioxime. This was subjected to the Beckmann rearrangement using Dziewonski and Spirer's procedure. Two products were isolated, one of which was readily soluble in glacial acetic acid and the other only very slightly soluble. The latter compound, m.p. 208–210°, had the composition of a monoacetate intermediate whereas the former compound, m.p. 300–301°, analyzed for a diacetamidoacenaphthene. This could not be hydrolyzed with dilute hydrochloric acid. Dziewonski and Spirer had reported a single product, m.p. 227–228°, which is reported to be hydrolyzed with 6% hydrochloric acid to give 5,6-diaminoacenaphthene.

When the monoacetate intermediate was again subjected to the conditions of the Beckmann rearrangement using twice the volume of solvent, the diacetamide, m.p. 300–301°, was formed. This diacetamidoacenaphthene XI was synthesized from 3,6-diaminoacenaphthene (VII). A mixture of this compound and the diacetamidoacenaphthene from the rearrangement of the dioxime of diacetylacenaphthene obtained by direct acylation melted without depression and their infrared spectra were superimposable. Thus the diacetylacenaphthene melting at 149° is the 3,6-isomer X and not the 5,6-isomer as reported by Dziewonski and Spirer. The diacid, prepared by the haloform reaction on this diacetylacenaphthene must then be the 3,6-isomer XII. It is not inconceivable that two diacetylacenaphthenes exist that melt at 149°, but due to the great difference in symmetry of the two isomers, it seems unlikely. Although Dziewonski and Spirer's preparation of the compound involved a much higher reaction temperature, they stated that their product was identical to the diacetylacenaphthene found by Fleischer and Wolff[16] who used a procedure similar to that used in this work.

During the course of the work, before the structure of the dibenzoyl derivative was established, it was assumed to be the 5,6-derivative and attempts were made to synthesize the products resulting from the rearrangement of the theoretically possible isomeric dioximes. The dioxime could exist as *syn,syn*-diphenyl-, *syn,anti*-diphenyl-, and *anti,anti*-diphenyl-dioximes. Under the conditions for a Beckmann rearrangement, these oximes could yield a dibenzamide, a benzamide-

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[13] M. Freund and K. Fleischer, *Ann.*, **399**, 222 (1913).

[14] G. Berger and S. C. J. Oliver, *Rec. trav. chim.*, **46**, 600 (1927).

[15] G. T. Morgan and H. A. Harrison, *J. Soc. Chem. Ind.*, **49**, 413 T (1930).

[16] K. Fleischer and P. Wolff, *Ber.*, **53**, 925 (1920).

anilide, and a dianilide respectively. The products prepared in this study included the dianilide of 3,6-acenaphthene dicarboxylic acid which was first presumed to be the 5,6-isomer, the 5,6-dibenzamide, and a benzamide-anilide. In the preparation of the benzamide-anilide, 5-acenaphthanilide was nitrated to form a nitroacenaphthanilide. The reaction of 5-acenaphthoyl chloride with *o*-nitroaniline and with *p*-nitroaniline formed two of the possible nitro anilides, neither of which was identical with the product obtained from the nitration of 5-acenaphthanilide. These results indicate that nitration of the anilide occurred on the unsubstituted ring of acenaphthene. The nitration product was reduced and converted into a benzamide. This benzamidoacenaphthanilide has properties strikingly similar to the product obtained by rearranging dibenzoylacenaphthene dioxime. Both compounds crystallized from 1-butanol as colorless plates and both compounds melt at 276–277°. However, a mixture of the two substances melted with a depression of more than 30°.

EXPERIMENTAL

3,6-Dibenzoylacenaphthene (IX). Acenaphthene (30.8 g., 0.200 mole) and 63.0 g. (0.451 mole) of freshly distilled benzoyl chloride were dissolved in 250 ml. of dry nitrobenzene. The stirred solution was cooled to 3° and 60.0 g. (0.448 mole) of powdered anhydrous aluminum chloride was added during the course of 1.5 hr. at such a rate that the temperature did not rise above 5°. The flask was packed in ice and allowed to warm up overnight. The dark solution was then maintained at 30° for 1 hr., at 40° for 1 hr., and finally at 50° for 1 hr. After cooling the solution to room temperature, it was hydrolyzed with ice and hydrochloric acid. The nitrobenzene was removed by steam distillation leaving a black tarry mass which hardened on cooling. The water was drained from the residue which was then extracted with 300 ml. of hot ethanol. This extract was filtered with the aid of a hot funnel. The dark brown filtrate deposited tan crystals on cooling. This extraction procedure was continued until the ethanol filtrates ceased depositing crystals. The combined crude crystals weighed 24.0 g. (33%) and melted at 145–148°. The yields in this preparation varied from 15% to 33%. Two recrystallizations from ethanol with charcoal gave colorless prisms, m.p. 148.5–149.5°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 85.95; H, 5.28.

2,5-Dibenzoylnaphthalic anhydride. To a solution of 1.07 g. (0.0030 mole) of 3,6-dibenzoylacenaphthene dissolved in 15 ml. of glacial acetic acid was added 1.5 g. (0.067 mole) of chromic anhydride dissolved in a minimum of water. The solution was heated at reflux for 1 hr. during which time a crystalline solid separated. After cooling the mixture, the solid was separated by filtration. There was thus obtained 0.72 g. (58%) of product, m.p. 245–249°, which was dissolved in 5% sodium hydroxide solution and filtered to remove the small amount of occluded chromium hydroxide which precipitated. The solution was acidified and the precipitated acid crystallized twice from glacial acetic acid. The anhydride separated as colorless crystals, m.p. 250–251°.

Anal. Calcd. for $C_{26}H_{14}O_5$: C, 76.84; H, 3.47. Found: C, 76.98; H, 3.32.

2,5-Dibenzoylnaphthalimide. One g. (0.0025 mole) of 2,5-dibenzoylnaphthalic anhydride, prepared as described above, was dissolved in 100 ml. of 5% sodium hydroxide solution. On cooling the sodium salt crystallized. Water was added to form a clear solution at room temperature which was then acidified with 10% hydrochloric acid to liberate the acid which separated as a white precipitate. The 2,5-dibenzoylnaphthalic acid lost water at about 105° to form the anhydride which then melted at 249–250°. A solution of 0.40 g. (0.00094 mole) of the diacid in 50 ml. of concentrated ammonium hydroxide was boiled for 1 hr. During this time a white solid precipitated. After cooling the mixture, the product was removed by filtration and washed with water. Crystallization from toluene gave white needles, m.p. 246–249°.

Anal. Calcd. for $C_{26}H_{15}NO_4$: N, 3.46. Found: N, 3.57.

3,6-Dibenzoylacenaphthene dioxime. To 200 ml. of ethanol was added 3.30 g. (0.00910 mole) of 3,6-dibenzoylacenaphthene, 4.5 g. (0.065 mole) of hydroxylamine hydrochloride, and 5.2 g. (0.13 mole) of sodium hydroxide dissolved in a minimum of water. After 3 hr. of heating at reflux, about 25 ml. of water was added to dissolve some precipitated salt. After cooling, the solution was filtered and acidified to *p*H 2. The cream colored precipitate was filtered with suction, washed with cold water, and dried. The crude product (3.44 g., 96.5%) melted at 268–272°. One crystallization from ethanol, followed by two recrystallizations from 1-butanol with decolorizing charcoal gave colorless crystals, m.p. 271–273°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: N, 7.14. Found: N, 7.19.

3,6-Dibenzamidoacenaphthene (VIII). To a solution of 75 ml. of glacial acetic acid and 38 ml. of acetic anhydride was added 7.20 g. (0.0184 mole) of 3,6-dibenzoylacenaphthene dioxime. Hydrogen chloride was passed through the solution. Within a few minutes, heat was given off and the solid dissolved forming an orange solution. After passing hydrogen chloride gas through the solution for 4 hr., the flask was stoppered and left overnight. A yellow oil separated. The solution and oil were poured into one liter of cold water causing precipitation of a cream colored solid. This was filtered, washed with water, and dried. There was obtained 7.1 g. (99%) of crude product, m.p. 273–277°. Crystallization from 1-butanol with decolorizing charcoal gave colorless plates, m.p. 276–277°. A warm solution of this compound in equal parts of glacial acetic acid and acetic anhydride was again saturated with hydrogen chloride and allowed to stand overnight. The solid which separated when the solution was diluted with water indicated no further reaction.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: N, 7.14. Found: N, 7.18.

Hydrolysis of 3,6-dibenzamidoacenaphthene with 70% sulfuric acid. A mixture was prepared from 0.50 g. (0.0013 mole) of 3,6-dibenzamidoacenaphthene and 25 ml. of 70% sulfuric acid. The mixture was heated at reflux which caused the solid to dissolve slowly and sublimed benzoic acid to crystallize in the condenser. After 30 min. the starting material had dissolved completely. The mixture was cooled and then diluted with 250 ml. of cold water. The benzoic acid was separated by filtration and after drying was found to amount to 0.13 g. (42%). The hydrolysis filtrate was made alkaline with 10% sodium hydroxide solution which caused a green color to form in the solution. This solution was extracted with four 50-ml. portions of ether which were combined and then evaporated leaving a yellow residue, m.p. 102–108°, (0.19 g., 52%). An ether solution of this substance formed a white solid precipitate when saturated with dry hydrogen chloride. The amine was regenerated by adding 10% sodium carbonate solution to a water solution of the amine hydrochloride. Crystallization of the crude amine from petroleum ether, b.p. 60–70°, produced long, nearly colorless needles, m.p. 115–116°, of what is probably 3-benzamido-6-aminoacenaphthene.

Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.50. Found: C, 79.27; H, 6.05.

To a solution of 0.10 g. (0.00035 mole) of 3-benzamido-6-aminoacenaphthene, obtained as described above, in 5 ml. of dry pyridine was added 10 drops of benzoyl chloride. The brown solution was allowed to stand for 15 min. and then poured into 400 ml. of cold water. The cream colored precipitate was removed by filtration, washed with water, and dried. The yield of the product, m.p. 270–275°, was quantitative. A mixture of this compound and the product obtained by rearranging the 3,6-dibenzoyldioxime melted without depression. The infrared spectra of these two substances were identical.

Hydrolysis of 3,6-dibenzamidoacenaphthene (VIII) *with 100% phosphoric acid.* The product from the Beckmann rearrangement of the dioxime of 3,6-dibenzoylacenaphthene (3.50 g., 1.00 mole) was added to 25 g. of 100% phosphoric acid and hydrolyzed as described by Berger and Oliver.[14] The yield of crude benzoic acid that sublimed from the reaction mixture was 1.58 g. which was dissolved in dilute sodium hydroxide and reprecipitated. The weight of the purified benzoic acid was 1.33 g. (1.22 mole). The phosphoric acid filtrate was made alkaline with 10% sodium hydroxide and extracted with five 50-ml. portions of ether. After drying, the combined ether solution was saturated with dry hydrogen chloride which precipitated the salt of the amine. The amine hydrochloride was converted into the amine by dissolving it in warm water and adding 10% sodium carbonate solution. The cream colored amine, m.p. 100–101° weighed 0.94 g. (0.37 equivalent).

3,6-Diacetylacenaphthene (X). To 400 ml. of dry carbon disulfide was added 75.0 g. (0.955 mole) of freshly distilled acetyl chloride and 60.0 g. (0.390 mole) of acenaphthene. The solution was cooled to 3° and 140 g. (1.05 mole) of powdered anhydrous aluminum chloride was added slowly so that the temperature did not rise above 5°. After packing the flask in ice, the solution was left to warm to room temperature overnight. During this time a tarry reddish brown mass separated which made stirring very difficult. The carbon disulfide was decanted and the residue was hydrolyzed with ice and hydrochloric acid producing a black solid. The solid was separated by filtration and partially dried on the suction filter, and then extracted with 400 ml. of boiling ethanol which deposited crude crystals on cooling. The extractions were continued until no crystals formed. The crude product was recrystallized from ethanol with decolorizing charcoal to yield 17.3 g. (19%) of a light tan crystalline product, m.p. 146–148°. Two additional recrystallizations from ethanol gave a white product, m.p. 148–149° (lit. 146°,[16] reported[10] as 5,6-diacetylacenaphthene, m.p. 149°).[17]

3,6-Acenaphthenedicarboxylic acid (XII). To a solution of 500 ml. of Chlorox (5.25% sodium hypochlorite) and 50 ml. of 10% sodium hydroxide was added 10.0 g. (0.042 mole) of 3,6-diacetylacenaphthene (X). The mixture was warmed for 3 hr. after which an additional 100 ml. of Chlorox was added. Two hours at reflux gave a clear pale yellow solution which was cooled and the excess sodium hypochlorite destroyed by adding sodium bisulfite. Acidification with concentrated hydrochloric acid to *p*H 2 caused precipitation of a cream colored solid which was removed by filtration, washed with water, and dried. The crude product, 10.1 g. (97%) which did not melt below 340° was crystallized from glacial acetic acid.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 68.63; H, 4.04.

3,6-Diacetylacenaphthene dioxime. This compound was prepared in 84% yield by the method of Dziewonski and Spirer,[10] m.p. 206–208° (lit.[10] reported as 5,6-diacetylacenaphthene dioxime, m.p. 196–197°). The product was crystallized from benzene.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: N, 10.44. Found: N, 10.20.

3,6-Diacetamidoacenaphthene (XI). A solution was prepared of 2.0 g. (0.0075 mole) of 3,6-diacetylacenaphthene dioxime in 10 ml. of glacial acetic acid and 15 ml. of acetic anhydride. Hydrogen chloride was passed through the pale orange solution for 2 hr. After the first 15 min., precipitation of a cream colored solid began. The flask was stoppered and allowed to stand for 3 hr. The solid was removed by filtration and washed with water. The crude product, m.p. 185–204°, amounted to 0.93 g. Several crystallizations from ethanol with decolorizing charcoal gave colorless crystals, m.p. 208–210°. Analyses indicate an acetate intermediate probably 6-acetamido-3-acetylacenaphthene oxime acetate.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.54; H, 5.92; N, 9.20.

The filtrate from the above separation was poured into 400 ml. of cold water. A tan solid separated which was removed by filtration and washed with water. This substance (0.56 g.) melted at 295–299°. Two crystallizations from ethanol with decolorizing charcoal gave colorless needles, m.p. 299–301° (block). The analysis indicates a diacetamidoacenaphthene.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: N, 10.44. Found: N, 10.46.

The oxime acetate was dissolved in 50 ml. of a cold solution of equal volumes of glacial acetic acid and acetic anhydride. Hydrogen chloride was passed through the brown solution for 5 hr. The solution became warm and within 20 min. a cream colored solid began to precipitate. The flask was stoppered and allowed to stand overnight. The mixture was poured into a liter of water and filtration of the aqueous mixture separated the product. The yield of crude product, m.p. 295–299°, was quantitative. Crystallization from ethanol and from toluene with decolorizing charcoal gave fine white needles of 3,6-diacetamidoacenaphthene (XI), m.p. 299–300°.

3-Nitroacenaphthene. Morgan and Harrison[15] reported two methods for preparing this compound. Our attempt with the benzoyl nitrate method gave only 5-nitroacenaphthene. By using the diacetylorthonitric acid the yellow-green solid, m.p. 140–145° was prepared in 17% yield (lit.[15] 151.5°).

3,6-Dinitroacenaphthene. This compound was prepared from 3-nitroacenaphthene as described in the literature. The crude yellow solid, m.p. 196–202°, was produced in 94% yield. Crystallization from glacial acetic acid gave yellow needles, m.p. 205–207° (lit.[15] 205–206°).

3,6-Diaminoacenaphthene (VII). Four grams (0.016 mole) of 3,6-dinitroacenaphthene, 200 mg. of 10% palladium-on-charcoal, and 75 ml. of ethanol were placed in a Parr hydrogenation bottle. A hydrogen pressure of 2.82 atm. was applied for 1 hr. The initially yellow mixture changed to a gray colored solution which was filtered to remove the catalyst. The filtrate exhibited a strong blue fluorescence. The ethanol was removed by warming the solution under reduced pressure and the gray residue, (2.92 g., 98%) m.p. 95–99°, crystallized from petroleum ether, b.p. 60–70°, formed very pale yellow needles, m.p. 99–100°. This diamine did not depress the melting point of the diamine obtained by the hydrolysis of 3,6-dibenzamidoacenaphthene (VIII).

Anal. Calcd. for $C_{12}H_{12}N_2$: N, 15.21. Found: N, 15.17.

3,6-Dibenzamidoacenaphthene (VIII) *from the diamine* VII. To 1.82 g. (0.0100 mole) of VII in 15 ml. of dry pyridine was added 2.81 g. (0.0200 mole) of benzoyl chloride. The brown solution was allowed to stand for 30 min. When the solution was poured into a liter of cold water a cream colored precipitate separated. This was collected on a filter, washed well with water and dried. The crude product, m.p. 263–274°, 3.68 g. 94%, was crystallized several times from 1-butanol with decolorizing charcoal yielding colorless plates, m.p. 277–279°.

3,6-Diacetamidoacenaphthene (XI) *from the diamine* VII. A solution was prepared from 0.91 g. (0.0050 mole) of VII in 10 ml. of pyridine. To this solution was added dropwise 1.0 g. (0.010 mole) of acetic anhydride. After about 10 min., tan crystals began to deposit. After standing for 45 min., the mixture was poured into one liter of cold water. The

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[17] An improved procedure for the preparation of this compound was described by A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **22**, 1197 (1957) after completion of this work. These authors assumed the formation of the 5,6-isomer.

tan suspension was filtered and the resulting solid washed with water and dried. The crude product, m.p. 290–295°, 1.13 g. (84%), was crystallized from ethanol with decolorizing charcoal and again from toluene, m.p. 299–300°.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: N, 10.44. Found: N, 10.61.

5,6-Dibenzamidoacenaphthene (V). To 1.1 g. (0.0060 mole) of III[6] in 20 ml. of dry pyridine was added 1.7 g. (0.12 mole) of benzoyl chloride. After 30 min. at room temperature, the solution was poured into 600 ml. of cold water causing the precipitation of a cream colored solid. The solid was removed by filtration, washed well with water, and dried. The crude product, m.p. 268–272°, weighed 1.95 g. (82%). It was crystallized from glacial acetic acid with decolorizing charcoal, forming very pale yellow needles, m.p. 275–276°.[6]

A mixture of this compound and the product from the Beckmann rearrangement of the dioxime of the dibenzoylacenaphthene obtained by the benzoylation of acenaphthene with the Friedel-Crafts reaction melted below 230°.

3,6-Acenaphthenedicarboxanilide. A mixture of 1.00 g. (0.00414 mole) of the 3,6-dicarboxylic acid XII and 15 ml. of thionyl chloride was heated at reflux for a total of 15 hr. During this period the solid dissolved forming a dark solution. The excess thionyl chloride was removed under reduced pressure and the acid chloride dissolved in dry benzene and 0.79 g. (0.0085 mole) of freshly distilled aniline in 25 ml. of benzene was added. A precipitate formed which was filtered off and washed well with water. The tan product, m.p. 287–294°, 1.15 g. (71%) was crystallized from 1-butanol and from chloroform with charcoal forming colorless crystals, m.p. 302–304°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: N, 7.14. Found: N, 7.27.

5-Acenaphthanilide. To 8.0 g. (0.040 mole) of 5-acenaphthoic acid there was added 50 ml. of dry benzene and 10 ml. of thionyl chloride. The mixture was warmed for 3 hr. on the steam bath, during which time the solid dissolved to form a dark solution. The solvent was removed by warming the solution under reduced pressure. The tan acid chloride was dissolved in 25 ml. of dry benzene and to this solution was added 7.5 g. (0.081 mole) of freshly distilled aniline dissolved in 25 ml. of dry benzene. Aniline hydrochloride separated as a white precipitate. The mixture was warmed on the steam bath for 5 min. and then filtered. The brown benzene solution deposited tan crystals on cooling. This product was separated by filtration, washed with a little benzene, and dried, m.p. 165–169°. The yield was 8.3 g. (74%). Further recrystallization from benzene and finally from cyclohexane gave fine colorless needles, m.p. 173–174°.

Anal. Calcd. for $C_{19}H_{15}NO$: N, 5.13. Found: N, 4.96.

Nitration of 5-acenaphthanilide. A mixture of 11.5 g. (0.0422 mole) of 5-acenaphthanilide and 100 ml. of glacial acetic acid was warmed on the steam bath to 80°. The solid was only slightly soluble at that temperature. After the mixture had cooled to 55°, concentrated nitric acid (23 ml., d. 1.42) was added rapidly with stirring. The temperature rose to 61° and the solid dissolved completely forming a brown solution. The solution was cooled to room temperature and then diluted with two liters of cold water. The yellow precipitate was collected on a filter, washed well with water, and dried. The crude product, 10.8 g., melted below 100°. Crystallization from benzene with decolorizing charcoal gave 2.70 g. (20%) of pale yellow needles melting at 250–253°. Several recrystallizations from the same solvent gave a product, m.p. 255–257°. The position of the nitro group has not been established and the compound is therefore designated 3(5)-nitro-6-acenaphthanilide.

Anal. Calcd. for $C_{19}H_{14}N_2O_3$: N, 8.80. Found: N, 8.51.

Evaporation of the benzene filtrates gave 6.4 g. of a brown oil which could not be crystallized.

N-(o-Nitrophenyl)-5-acenaphthamide. A mixture, prepared from 10 ml. of thionyl chloride and 1.0 g. (0.0050 mole) of 5-acenaphthoic acid was heated under reflux for 2 hr. The solid dissolved during this period. After removing the excess thionyl chloride by warming under reduced pressure, the acid chloride was dissolved in 10 ml. of dry benzene. A solution of 1.38 g. (0.0100 mole) of *o*-nitroaniline in 30 ml. of dry benzene was added and the dark solution warmed on the steam bath for 10 min. The benzene was removed and the product crystallized from ethanol with decolorizing charcoal. The bright yellow needles, m.p. 198–200°, weighed 0.53 g. (33%). One recrystallization from ethanol raised the melting point to 199–200°.

Anal. Calcd. for $C_{19}H_{14}N_2O_3$: N, 8.80. Found: N, 8.75.

N-(p-Nitrophenyl)-5-acenaphthamide. To 1.0 g. (0.0050 mole) of 5-acenaphthoic acid was added 10 ml. of thionyl chloride. This mixture was heated at reflux for 2 hr., during which time the solid dissolved to give a brown solution. The excess thionyl chloride was removed by warming the solution under reduced pressure. After dissolving the solid acid chloride in 10 ml. of dry benzene, *p*-nitroaniline (1.38 g., 0.00100 mole) dissolved in 50 ml. of dry benzene was added. The solution was warmed on the steam bath for 5 min. and then cooled. Since no product separated, the volume of the solution was reduced to about 20 ml. Brown crystals deposited slowly. These were removed by filtration, washed with a little benzene, and dried. The crude product, m.p. 230–238°, amounted to 0.87 g. (55%). Recrystallization from toluene and finally from benzene with decolorizing charcoal gave long, pale yellow needles, m.p. 236–238°.

Anal. Calcd. for $C_{19}H_{14}N_2O_3$: N, 8.80. Found: N, 8.15.

A mixture of this compound and the product of the nitration of 5-acenapthanilide (m.p. 255–257°) melted at 208–220°.

3(5)-Amino-6-acenaphthanilide. The product from the nitration of 5-acenaphthanilide (1.60 g., 0.0050 mole) was suspended in 50 ml. of ethanol in a carefully cleaned hydrogenation bottle. About 200 mg. of 10% palladium-on-charcoal catalyst was added and the bottle was flushed three times with hydrogen. The hydrogen pressure was brought up to 3.1 atm. After shaking for 40 hr., the pressure had dropped to 2.7 atm. and the color had changed from yellow to green. The product was filtered off and dried. The yield of amine, m.p. 204–207°, was quantitative. Crystallization from cyclohexane with decolorizing charcoal gave colorless micro needles, m.p. 209–210°.

Anal. Calcd. for $C_{19}H_{16}N_2O$: N, 9.72. Found: N, 9.70.

3(5)-Benzamido-6-acenaphthanilide. To 0.72 g. (0.0025 mole) of 3(5)-amino-6-acenaphthanilide, obtained by reduction to the product of the nitration of 5-acenaphthanilide, dissolved in 10 ml. of dry pyridine was added 0.35 g. (0.0025 mole) of benzoyl chloride. The dark solution was allowed to stand for 30 min. and then poured into 400 ml. of cold water. A cream colored precipitate formed which was removed by filtration, washed with water, and dried. The yield of benzamide, m.p. 273–275° was quantitative. Three recrystallizations of the crude product from butanol with decolorizing charcoal gave nearly colorless plates, m.p. 276–277°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: N, 7.14. Found: N, 7.10.

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