2-Carbethoxy-5-methylcyclohexanone and Aniline.—the keto ester (0.05 mole) and aniline (0.125 mole) were heated together in a flask equipped with an air-cooled condenser in an oil-bath at 190° for five hours. The DPU crystallized as the reaction mixture cooled; after washing with ether, it weighed 5.60 g. (52.8%). The filtrate and washings were extracted with 5% hydrochloric acid and the ether solution was dried and distilled. The residue was distilled at 90 mm. pressure, but only a small amount of material distilled so that no accurate boiling temperature could be observed. A sample of the distillate was treated with 2,4-dinitrophenylhydrazine and gave the 3-methylcyclohexanone derivative, m. p. 158–160°, after repeated recrystallization.

β-Aminocrotonanilide and Aniline.—It was found that a vigorous evolution of ammonia ensued when these reagents were heated, so the apparatus was modified so that a delivery tube led from the top of the distilling column to beneath the surface of cold standard (1.783 *N*) sulfuric acid solution. Titration of the acid solution with sodium hydroxide indicated the absorption of 92.6% of the possible amount of ammonia after the reaction mixture had been heated six hours. The yield of DPU was 91.8%.

Cyanoacetanilide and Aniline.—When cyanoacetanilide was heated with aniline in the usual way for six hours, very low yields (6–7%) of DPU were obtained along with much lower-melting material which was hydrolyzed by dilute hydrochloric acid. The small amount of distillate collected in the Dry Ice-trap was apparently ammonia.

Two 24-hour-heated runs were then made. In the first, the distillate was mixed with 30% sulfuric acid and the mixture was heated and then distilled. From the distillate, a very small amount of the *p*-nitrobenzyl ester of acetic acid was obtained in the usual way. This may have come from the hydrolysis of acetonitrile, the expected cleavage product. The yield of pure DPU obtained in this experiment was *ca.* 40%. In the second 24-hour experiment, the ammonia evolved was absorbed in standard acid solution and determined by back titration; it amounted to 36.3%: The yield of DPU was 55.5%. Some high-melting (> 310°) material was also isolated but was not identified.

Summary

It has been shown that acetoacetic ester reacts with aniline in a manner analogous to the "ketone cleavage" of this ester by dilute aqueous alkali, producing *sym*-diphenylurea and acetone. In addition, acetone anil is produced, indicating that some reaction of the keto group with aniline precedes cleavage. Acetoacetanilide and acetoacetic ester anil react with aniline under the same conditions to give *sym*-diphenylurea in comparable yields. Some other structurally related esters and anilides have been shown to undergo cleavage by aniline in similar fashion. Factors which influence the ratio of acetone/acetone anil produced are discussed.

AUSTIN, TEXAS RECEIVED JUNE 1, 1950

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

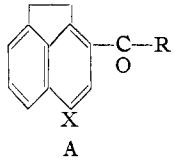
The Acylation of 5-Bromo- and 5-Chloroacenaphthene by the Friedel–Crafts Procedure[1,2]

BY DOROTHY V. NIGHTINGALE AND ROBERT M. BROOKER

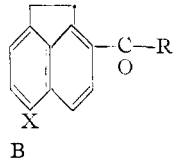
In a previous publication[3] it was stated that the reaction of 5-chloroacenaphthene with acetyl chloride in the presence of aluminum chloride as the catalyst yielded two isomeric acetylchloroacenaphthenes, but their orientation was not determined.

It has now been established that the two ketones are 3-acetyl-5-chloroacenaphthene, I-A and 3-acetyl-6-chloroacenaphthene, I-B. Acetylation of 5-bromoacenaphthene and benzoylation of both 5-chloro- and 5-bromoacenaphthene likewise yielded analogous pairs of ketones with the acyl group in the 3-position.[4]

The two acetylchloroacenaphthenes were first separated from the reaction product by fractional crystallization from ether and chloroform with high losses. In the present research it was found that oximation of the crude methyl



A



B

I-A, R = CH_3, X = Cl IB, R = CH_3, X = Cl
II-A, R = CH_3, X = Br II-B, R = CH_3, X = Br
III-A, R = C_6H_5, X = Cl III-B, R = C_6H_5, X = Cl
IV-A, R = C_6H_5, X = Br IV-B, R = C_6H_5, X = Br

ketones, fractional crystallization of the oximes and hydrolysis of the pure oximes to the ketones was more rapid and gave better yields.

A comparison of the ultraviolet absorption spectra of the methyl ketones with the published spectra[5] of 3-acetylacenaphthene and 5-acetylacenaphthene indicate that the acetyl groups are in the 3-position. The spectra of the acetylhaloacenaphthenes closely resemble the spectrum of 3-acetylacenaphthene and are notably different from the spectrum of 5-acetylacenaphthene (Figs. 1, 2, 3 and 4).

The methyl ketones were oxidized to the corresponding 5-halo- and 6-halo-3-acenaphthoic acids and their ultraviolet absorption spectra closely resemble the published spectrum of 3-acenaph-

(1) From the Ph.D. thesis of Robert M. Brooker, June, 1950.

(2) Presented in part at the St. Louis Meeting of the American Chemical Society, September, 1948.

(3) Nightingale, Ungnade and French, THIS JOURNAL, **67**, 1262 (1945).

(4) C. F. Roney (Masters Dissertation, University of Missouri, 1948) first separated 3-acetyl-5-bromo- and 3-acetyl-6-bromoacenaphthene by fractional crystallization of the crude ketones from a mixture of chloroform and ether. He converted the pure ketones to their oximes, but did not isolate pure acetylated amines from the product of the Beckmann rearrangement of the oximes.

(5) Jones, THIS JOURNAL, **67**, 2127 (1945).

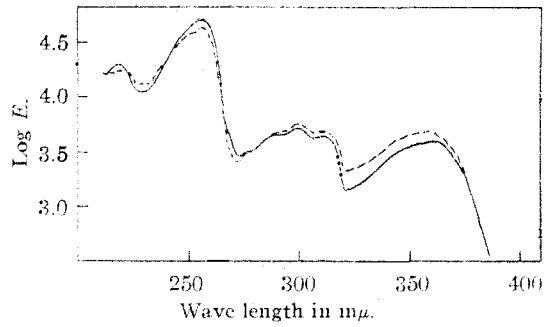


Fig. 1.—Ultraviolet absorption spectra: ——, 3-acetyl-6-bromoacenaphthene; – – – –, 3-acetyl-5-bromoacenaphthene.

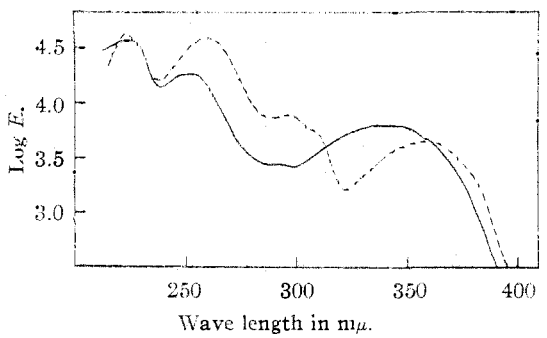


Fig. 2.—Ultraviolet absorption spectra: ——, 5-benzoylacenaphthene; – – – –, 3-benzoylacenaphthene.

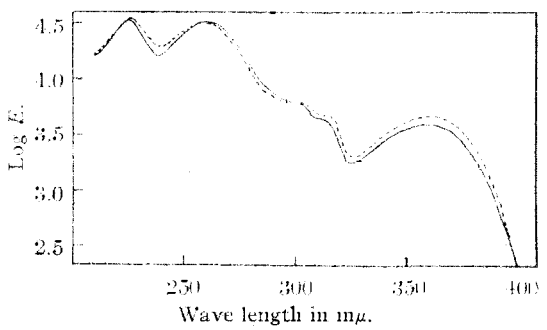


Fig. 3.—Ultraviolet absorption spectra: ——, 3-benzoyl-6-bromoacenaphthene; – – – –, 3-benzoyl-5-bromoacenaphthene.

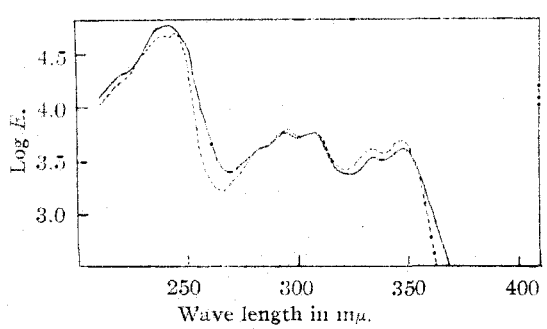


Fig. 4.—Ultraviolet absorption spectra: ——, 6-bromo-3-acenaphthoic acid; – – – –, 5-bromo-3-acenaphthoic acid.

thoic acid[5] and differ notably from the spectrum of 5-acenaphthoic acid (Fig. 5).

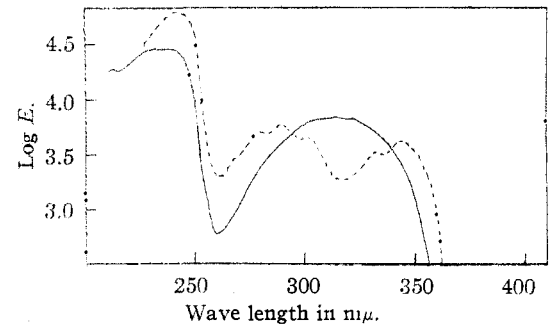
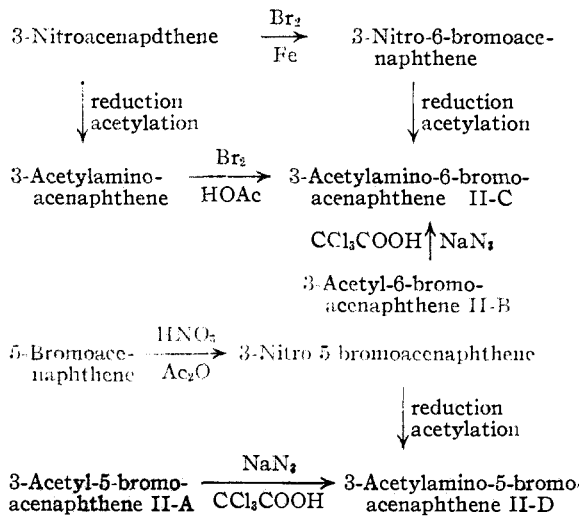


Fig. 5.—Ultraviolet absorption spectra: ——, 5-acenaphthoic acid; – – – –, 3-acenaphthoic acid.

The orientation of these ketones was determined by the following series of reactions illustrated with the bromoacenaphthene compounds



The known 6-acetylamino-5-bromoacenaphthene was prepared[6] but it depressed the melting points of both II-C and II-D.

3-Nitro-6-bromoacenaphthene has been prepared by the bromination of 3-nitroacenaphthene in acetic acid solution[7] but bromination in carbon tetrachloride with iron (by hydrogen) as the catalyst gave a better yield of product. The 3-acetylamino-6-bromoacenaphthene obtained from this nitro compound did not depress the melting point of II-C obtained from 3-acetyl-6-bromoacenaphthene, II-B. Bromination of 3-acetylaminoacenaphthene in acetic acid solution also gave II-C. The fact that 3-nitroacenaphthene and 3-acetylaminoacenaphthene both brominate in the same position is unusual.

The haloacenaphthene ketones were converted

(6) Dziewonski, Schoen and Glazner, *Bull. intern. acad. polon. sci.*, 1929A, 636; *C. A.*, **25**, 1518 (1931).

(7) Campbell, Anderson and Gilmore, *J. Chem. Soc.*, 446 (1940). The structure of this compound has not been rigorously proved, but is probably correct.

to the corresponding acylated amines by the Schmidt reaction using the procedure of Dice and Smith[8] rather than by the Beckmann rearrangement of the ketoximes.

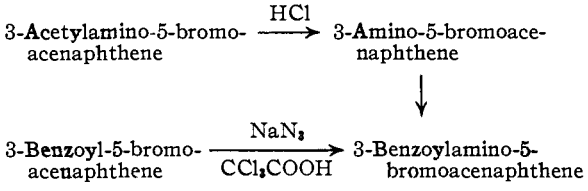
Dziewonski, Schoen and Glazner[6] nitrated 5-bromoacenaphthene with nitric acid in acetic acid and isolated 5-nitro-6-bromoacenaphthene along with small amounts of another mono nitro compound which they did not identify.

When 5-bromoacenaphthene was nitrated with nitric acid in acetic anhydride under carefully controlled conditions, 3-nitro-5-bromoacenaphthene was easily isolated. This nitro compound yielded an acetylamino compound identical with II-D obtained from the Schmidt reaction of the ketone II-A. It would appear that Dziewonski's unidentified nitro compound was the 3-nitro-5-bromoacenaphthene.

The nitration of 5-chloroacenaphthene under the same conditions yielded 3-nitro-5-chloroacenaphthene, which was converted to 3-acetylamino-5-chloroacenaphthene, identical with the acetylamino compound obtained from ketone I-A.

4-Nitroacenaphthene was obtained by diazotization of 4-nitro-5-aminoacenaphthene with sulfuric acid and ethyl alcohol. Morgan and Stanley[9] had attempted to synthesize this compound by diazotization of 4-nitro-5-aminoacenaphthene in aqueous solution but were unsuccessful.

The structures of the benzoylhaloacenaphthenes were determined by converting them to the benzoylaminohaloacenaphthenes, which were identical with the benzoyl derivatives obtained from the 3-amino-5-halo- and 3-amino-6-haloacenaphthenes



The structures of the two acetylchloroacenaphthenes, I-A and I-B, and the two benzoylchloroacenaphthenes, III-A and III-B, were assigned by analogy with the bromo compounds. Their ultraviolet absorption spectra are very similar to the spectra of II-A, II-B, IV-A and IV-B, respectively.

Experimental[10]

5-Bromoacenaphthene was prepared by bromination of acenaphthene according to the procedure of Dashevski and Karishin[11] except that 95% alcohol or absolute alcohol was used as the solvent instead of 75% alcohol, to facilitate the smooth distillation of the reaction product.

5-Chloroacenaphthene was prepared by chlorination of acenaphthene with sulfuryl chloride according to the procedure of Crompton and Walker.[12]

3-Benzoylacenaphthene was obtained from the reaction of phenylmagnesium bromide and 3-acenaphthamide by the method of Fieser and Cason.[13]

The Acylations.—All of the acetylations and benzoylations were done in nitrobenzene solution by the previously described procedure for the preparation of the acetyl-5-chloroacenaphthenes[8]

When acetyl-5-bromoacenaphthene was distilled, the fraction distilling at 205–210° (3 mm.) was collected and was a mixture from which the two isomeric ketones were obtained in the following manner: the distillate (15 g.) dissolved in 250 cc. of alcohol was refluxed for two hours on a water-bath with 8 g. of hydroxylamine hydrochloride and 15 g. of sodium hydroxide in 50 cc. of water. When the solution was poured into 1500 cc. of water, the solid oximes separated and were removed by filtration. Fractional crystallization of this solid from aqueous alcohol yielded the two pure oximes (Table I), which were converted to their respective ketones by refluxing with a 1:1 aqueous solution of hydrochloric acid.

The crude ketone fraction from the benzoylation of 5-bromoacenaphthene was collected at 240–270° (4–5 mm.). Fractional crystallization of this product from a 1:2.5 mixture of ether and chloroform yielded the two pure ketones.

The mixture of isomeric acetyl-5-chloroacenaphthenes was separated readily by conversion to the oximes as described above.

The mixture of benzoyl-5-chloroacenaphthenes, b. p. 262–264° (5 mm.), was separated by fractional crystallization from chloroform and ether. Neither 3-benzoyl-5-chloronaphthene nor 3-benzoyl-5-bromoacenaphthene would form oximes by any of the usual procedures.

Hydrolysis of the oxime of 5-benzoylacenaphthene yielded the ketone and 5-benzoylaminoacenaphthene, m. p. 210–211°, which did not depress the melting point of an authentic sample of 5-benzoylaminoacenaphthene.

The physical constants of the haloacenaphthene ketones and their oximes are listed in Table I.

Conversion of the Ketones to the Acylated Amines by Means of Sodium Azide (Schmidt Reaction).—The procedure of Dice and Smith[8] was followed in detail. It was necessary to add three to five drops of concd. sulfuric acid to the trichloroacetic acid to promote the reaction of the 3-benzoyl-5-haloacenaphthenes. The physical constants and analyses of the acylated amines are listed in Table II. The acetylamino compounds were hydrolyzed by means of alcoholic hydrochloric acid. The amine hydrochlorides were stable but the free amines darkened rapidly and were not purified for analysis but were used at once for conversion to benzoyl derivatives or reconversion to the acetyl derivatives. The benzoylaminohaloacenaphthenes were hydrolyzed very slowly, if at all, even after long refluxing with alcoholic hydrochloric acid.

Synthesis of the Nitro Compounds.—Acenaphthene, 5-bromoacenaphthene and 5-chloroacenaphthene were nitrated in acetic anhydride solution essentially according to the directions of Morgan and Harrison[14] for the preparation of 3-nitroacenaphthene. 3-Nitro-5-bromoacenaphthene and 3-nitro-5-chloroacenaphthene crystallized from the nitration mixture when the final temperature was held at 16° for about fifteen minutes whereas 3-nitroacenaphthene crystallized at 13°.

3-Nitro-5-bromoacenaphthene was obtained in 28% yield and melted at 179–180° after crystallization from alcohol.

Anal. Calcd. for $C_{12}H_8NO_2Br$: C, 51.83; H, 2.90. Found: C, 52.08; H, 2.90.

The filtrate from the nitration was diluted with about five times its volume of water and the separated solid was collected on a filter. This solid was recrystallized from

(8) Dice and Smith, *J. Org. Chem.*, **14**, 179 (1949).

(9) Morgan and Stanley, *J. Soc. Chem. Ind.*, **43**, 343T (1924).

(10) The carbon and hydrogen analyses were done by K. T. Zilch, R. A. Carpenter, J. S. Finney and R. M. Brooker.

(11) Dashevski and Karishin, *Org. Chem. Ind.* (*U. S. S. R.*), **4** 106 (1937); *C. A.*, **32**, 2111 (1938).

(12) Crompton and Walker, *J. Chem. Soc.*, **101**, 958 (1912).

(13) Fieser and Cason, THIS JOURNAL, **61**, 1740 (1939).

(14) Morgan and Harrison, *J. Soc. Chem. Ind.*, **49**, 413T (1930).

TABLE I

THE ACENAPHTHENE KETONES AND THEIR OXIMES

Acenaphthene ketone	Yield, %	M. p., °C.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
3-Acetyl-6-bromo-[a]	50	91.5–92	$C_{14}H_{11}OBr$	61.09	61.07	4.03	4.28
3-Acetyl-5-bromo-[a]	25	152–153	$C_{14}H_{11}OBr$	61.09	61.26	4.03	4.30
3-Benzoyl-6-bromo	23.3	110–111	$C_{19}H_{13}OBr$	67.67	67.92	3.88	3.78
3-Benzoyl-5-bromo-	9.3	138–139	$C_{19}H_{13}OBr$	67.67	67.80	3.88	3.71
3-Benzoyl-6-chloro-	24.7	106–107	$C_{19}H_{13}OCl$	77.95	77.90	4.48	4.48
3-Benzoyl-5-chloro-	11.8	141–142	$C_{19}H_{13}OCl$	77.95	77.99	4.48	4.33
OXIMES OF THE KETONES							
3-Acetyl-6-bromo-[a]	95	184–185	$C_{14}H_{12}ONBr$	57.93	58.15	4.14	4.34
3-Acetyl-5-bromo-[a]	95	164–165	$C_{14}H_{12}ONBr$	57.93	57.91	4.14	4.43
3-Acetyl-6-chloro-	90	183–184	$C_{14}H_{12}ONCl$	68.43	68.61	4.92	5.01
3-Acetyl-5-chloro-	91	140–141	$C_{14}H_{12}ONCl$	68.43	68.29	4.92	4.97
3-Benzoyl-6-bromo-	90	186–187	$C_{19}H_{14}ONBr$	64.78	64.90	4.00	4.32
3-Benzoyl-6-chloro-	88	189–190	$C_{19}H_{14}ONCl$	74.14	74.17	4.60	4.58

[a] Reported by C. F. Roney, ref. 4.

TABLE II

THE ACYLAMINOACENAPHTHENES

Acenaphthene derivative	Yield, %	M. p., °C.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
5-Benzoylamino-	62.0	210–211[a]					
3-Acetylamino-6-bromo-	72.3	206–207	$C_{14}H_{12}NOBr$	57.93	57.77	4.13	4.19
3-Acetylamino-5-bromo	70.3	213–214	$C_{14}H_{12}NOBr$	57.93	57.84	4.13	4.18
3-Acetylamino-6-chloro	73.5	207–208	$C_{14}H_{12}NOCl$	68.45	68.32	4.92	4.75
3-Acetylamino-5-chloro	71.5	210–211	$C_{14}H_{12}NOCl$	68.45	68.27	4.92	4.82
3-Benzoylamino-6-bromo	63.2	218–219	$C_{19}H_{14}NOBr$	64.78	65.04	4.00	4.07
3-Benzoylamino-5-bromo	61.2	224–255	$C_{19}H_{14}NOBr$	64.78	64.49	4.00	4.22
3-Benzoylamino-6-chloro	59.0	213–214	$C_{19}H_{14}NOCl$	74.14	73.88	4.60	4.95
3-Benzoylamino-5-chloro	56.3	209–210	$C_{19}H_{14}NOCl$	74.14	73.97	4.60	4.38

[a] Reported by Graebe and Haas, *Ann.*, **327**, 91 (1903).

alcohol to yield 25.3 g. (50.6%) of a product melting at 120–125°. Repeated crystallization of this material failed to yield a pure compound. It was probably a mixture of 3-nitro-5-bromoacenaphthene and 5-nitro-6-bromoacenaphthene.

3-Nitro-5-chloroacenaphthene was obtained in 29% yield and melted at 169–170°.

Anal. Calcd. for $C_{12}H_8NO_2Cl$: C, 61.68; H, 3.45. Found: C, 61.90; H, 3.23.

The filtrate from this nitration was poured into five times its volume of water and the solid separated by filtration. Recrystallization from alcohol yielded 22.5 g. (44%) of a product, m. p. 138–140°. This material was probably a mixture of 3-nitro-5-chloroacenaphthene and 5-nitro-6-chloroacenaphthene which could not be separated.

3-Nitro-6-bromoacenaphthene was prepared as follows: 3-Nitroacenaphthene (2 g., 0.01 mole) was dissolved in 25 cc. of carbon tetrachloride and the solution was heated to boiling. Bromine (1.6 g., 0.01 mole) dissolved in 10 cc. of carbon tetrachloride was added and 0.5 g. of iron (Merck "iron by hydrogen") was stirred into the mixture. After standing at gentle reflux temperature with stirring, the hot solution was filtered to remove the iron and the 3-nitro-6-bromoacenaphthene crystallized from the cooled filtrate. The compound was recrystallized from alcohol and melted at 156–157°, the recorded value.[7] The yield was 1.4 g. (50%).

The ultraviolet absorption spectra of 3-nitro-6-bromoacenaphthene and 3-nitro-5-bromoacenaphthene are nearly identical with the absorption spectrum of 3-nitroacenaphthene.

Preparation of 4-Nitroacenaphthene.—4-Nitro-5-aminoacenaphthene[9] (1.5 g., 0.007 mole) was dissolved in 50 cc. of boiling alcohol. The solution was cooled to 5° and 20 cc. of concd. sulfuric acid was added at such a rate that the temperature did not exceed 20°. The solution was cooled to 10°, and 1.3 g. of sodium nitrite was added followed by 1.5 cc. of water. The temperature of the solution was allowed to rise to 20–25°, then cooled to 10° and another 1.5 g. portion of sodium nitrite was added. The temperature of the solution was allowed to rise to room temperature, then refluxed on a water-bath for three hours and poured into five volumes of water. The solid was collected on a filter, washed with water, then dissolved in alcohol and the solution treated with Norite. The 4-nitroacenaphthene separated from the cooled filtrate in yellow needles; m. p. 128–129°; yield, 0.2 g. (14%).

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.35; H, 4.55. Found: C, 72.60; H, 4.95.

The 4-nitroacenaphthene gave a light yellow color in concd. sulfuric acid.

The Synthesis of the Acetylaminohaloacenaphthenes.—The nitrohaloacenaphthenes were reduced with sodium hydrosulfite by the procedure of Morgan and Harrison.[14] The crude amines were unstable and were acylated at once with acetic anhydride.

The 3-acetylamino-5-bromoacenaphthene, m. p. 213–214°, did not depress the melting point of II-D obtained from II-A.

The 3-acetylamino-6-bromoacenaphthene, m. p. 206–207°, did not depress the melting point of II-C obtained from II-B.

The 3-acetylamino-5-chloroacenaphthene, m. p. 210–211°, did not depress the melting point of the acetylamino compound obtained from I-A.

3-Acetylamino-6-bromoacenaphthene was also synthesized in another manner. 3-Acetylaminoacenaphthene (1.4 g.) was dissolved in 20 cc. of glacial acetic acid and a solution of 0.9 g. of bromine in 7 cc. of glacial acetic acid was added slowly with stirring. The reaction temperature was maintained at 60° while the solution was stirred

an additional hour. As the solution cooled, crystals separated and were collected on a filter, washed with cold glacial acetic acid and finally with water. Recrystallization of the product from alcohol yielded 0.9 g. (56%) of 3-acetylamino-6-bromoacenaphthene, m. p. 206–207°, identical with II-C obtained from ketone II-B.

The Oxidation of the Acetylhaloacenaphthenes.—The ketones were oxidized with a hypochlorite solution prepared according to the procedure of Fieser and Cason[13] to yield the following acids: 5-Bromo-3-acenaphthoic acid, m. p. 304–305° dec.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.34; H, 3.27. Found: C, 56.16; H, 3.44.

6-Bromo-3-acenaphthoic acid, m. p. 289–290° dec.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.34; H, 3.27. Found: C, 56.26; H, 3.47.

5-Chloro-3-acenaphthoic acid, m. p. 279–280° dec.

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.10; H, 3.90. Found: C, 67.07; H, 4.15.

6-Chloro-3-acenaphthoic acid, m. p. 264–265° dec.

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.10; H, 3.90. Found: C, 66.95; H, 4.03.

The Ultraviolet Absorption Spectra.—The spectra were measured by Dr. E. E. Pickett, a spectroscopist at the University of Missouri, with a Beckman Model DU spectrophotometer. The quartz cells were 1.00 cm. thick. The spectra were measured against the solvent, 95% alcohol, in a similar cell.

Summary

5-Bromo- and 5-chloroacenaphthene have been acylated in nitrobenzene solution with acetyl chloride and benzoyl chloride in the presence of aluminum chloride. The product from each acylation was a mixture from which two ketones were isolated: the 3-acyl-5-halo- and the 3-acyl-6-haloacenaphthenes.

The bromination of 3-acetylaminoacenaphthene in acetic acid solution yielded 3-acetylamino-6-bromoacenaphthene.

COLUMBIA, MISSOURI RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thienol

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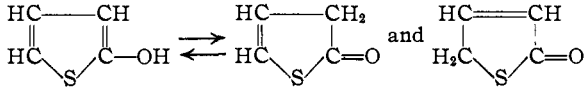
In the otherwise well-developed field of thiophene chemistry, the simple hydroxy derivative, 2-thienol,[2] is conspicuously absent; yet a survey of the literature shows but two attempts, both unsuccessful, toward its preparation.[3] Furthermore, while certain substituted thienols have been synthesized by ring-closure methods,[4] the introduction of the hydroxyl function into an existing thiophene nucleus has apparently not been recorded.

In the present work there is developed a preparative method for the simple thienols from thiophene, and a characterization of the more readily available isomer, 2-thienol.

The oxidation of aromatic Grignard reagents with oxygen ordinarily leads mainly to the formation of biaryls and tars. However, a modification involving the inclusion of a suitable aliphatic Grignard among the reactants has been found to repress these side-reactions, so that in the preparation of phenol by this method, the yield is increased from one-quarter to three-quarters of the theoretical.[5]

Analogous reactions have now been investigated for thiophene. Simple treatment of 2-thienylmagnesium bromide with oxygen was found to produce 2,2′-bithienyl in significant amounts, along with much hydrogen sulfide and resinous material, but no more than a trace of 2-thienol was formed. In the presence of somewhat more than an equivalent amount of isopropylmagnesium bromide these by-products were reduced sufficiently to permit isolation of the desired thienol in 25% yield.

2-Thienol is of considerable interest because it holds the possibility of enol–keto tautomerism, the "keto" forms being both 3- and 2-butenothiololactones



In general, compounds of the thiophene series exhibit a marked physical and chemical resemblance toward their benzene analogs. The extent to which 2-thienol resembles phenol, therefore, should depend on the tendency for it to exist in the enol form, which in turn is a measure of the aromatic character of the thiophene ring.

In the corresponding equilibrium for phenol, the ΔH value for the tautomeric shift from keto to enol has been estimated at approximately −16 kcal.[6]; this value is only slightly greater than the difference in resonance energies (10–12 kcal.) between the benzene and thiophene rings. Other things being equal, one might on this basis roughly predict nearly equal stabilities for the two tautomers of 2-thienol. This suggested dual nature has already been observed in substituted thienols.[4] It is reflected in the physical and

(1) The Texas Company Fellow, 1946–1948.

(2) The name "thienol" is based on the generally accepted use of the stem "thien" for the thienyl radical, C_4H_3S, analogous to the stem "phen" for the phienyl radical. Thus thienol and phenol are analogous terms, as are thienyl and phenyl. The name "2-thiophene-ol" (*cf. C. A.*, **39**, 5904 (1945)) obviously is poorly adapted for this substance, since thiophenol is generally used for C_4H_3SH.

(3) Thomas, *Compt. rend.*, **146**, 642 (1908); Mentzer and Billet, *Bull. soc. chim.*, **12**, 292 (1945).

(4) The simplest example, 5-methyl-2-thienol, is described by Steinkopf and Thormann, *Ann.*, **540**, 1 (1939).

(5) Kharasch and Reynolds, THIS JOURNAL, **65**, 501 (1943).

(6) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 291.