in 100 ml. of water, filtered, and neutralized with concentrated ammonia. After crystallization at 0° for twelve hours, 17.3 g. (91.2%) of α,δ-diaminoadipic acid was obtained. The product did not have a sharp melting point but sintered and charred at about 300°. It was soluble in acids and bases but insoluble in water.

B. By Treatment with Hydrazine.—A mixture of 4.64 g. of dimethyl α,δ-diphthalamidoadipate (m. p. 160–185°, 0.01 mole), 50 ml. of methanol and 1.2 ml. of an 85% aqueous hydrazine hydrate solution (0.02 mole) was heated under reflux for one hour. After cooling, 25 ml. of water was added and the methanol was removed by concentration under reduced pressure. Concentrated hydrochloric acid (25 ml.) was added to the residual aqueous suspension and the mixture was heated under reflux for one hour. After cooling to 0°, crystalline phthalhydrazide was removed by filtration. The filtrate was then concentrated under reduced pressure to remove most of the hydrochloric acid and the moist residue was dissolved in 50 ml. of water. A small amount of insoluble matter was removed by filtration and the clear filtrate was neutralized with 2 *N* sodium hydroxide. After cooling at 0° for twelve hours, 1.4 g. (79.5%) of α,δ-diaminoadipic acid was obtained.

Dimethyl α,δ-Diaminoadipate Dihydrochloride.—By the Fischer esterification method using methanol and hydrogen chloride, 15 g. of α,δ-diaminoadipic acid (from the acid hydrolysis) was converted to 21.2 g. (94%), m. p. 203–205° dec., of dimethyl α,δ-diaminoadipate dihydrochloride. A sample for analysis was obtained by recrystallization from methanol–ether; m. p. 206–207° dec.

Anal. Calcd. for $C_8H_{18}O_4N_2Cl_2$: C, 34.67; H, 6.55; N, 10.11. Found: C, 34.36; H, 6.59; N, 10.15.

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Metalation of Thianaphthene by *n*-Butyllithium

BY DAVID A. SHIRLEY AND MARGARET D. CAMERON[1]

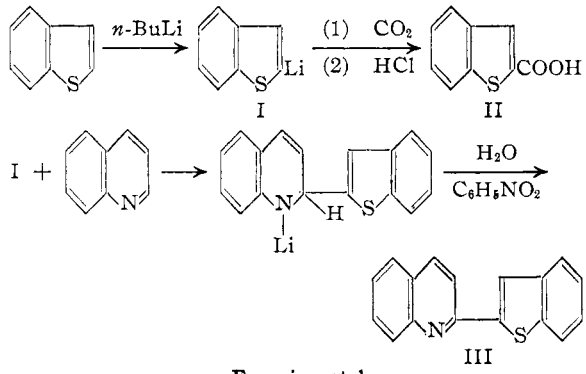
Thianaphthene previously has been metalated using ethylmagnesium bromide, sodamide, sodium metal and mercuric acetate. Weissgerber and Kruber[2] found that thianaphthene and ethylmagnesium bromide refluxed in dimethylaniline gave a 24% yield of the 2-derivative, and that sodamide and thianaphthene in xylene at 120° gave a 25–30% yield of each of the 2- and 2,3-sodio derivatives; Schönberg and co-workers[3] found that thianaphthene and powdered sodium in ether gave 2-thianaphthenylsodium in 56% yield after several days standing. Challenger and Miller[4] obtained the 2,3- and the 3-mercuric acetates by the action of mercuric acetate on thianaphthene.

In connection with a study of the chemistry of thianaphthene, its metalation with *n*-butyllithium was found to yield 54.6% 2-thianaphthenyllithium (I) after one hour at the temperature of refluxing ether. The position of the lithium substituent was determined by treatment of the thianaphthenyllithium with solid carbon dioxide followed by acidification to yield thianaphthene-2-carboxylic acid (II).

(1) Eli Lilly Research Fellow, 1949–1950.
(2) Weissgerber and Kruber, *Ber.*, **53**, 1551 (1920).
(3) Schönberg, Petersen and Kaltschmidt, *ibid.*, **66**, 233 (1933).
(4) Challenger and Miller, *J. Chem. Soc.*, 1005 (1939).

The 2-thianaphthenyllithium formed 2-(2′-thianaphthenyl)-quinoline (III) when treated with quinoline, hydrolyzed and the intermediate 1,2-dihydro-2-(2′-thianaphthenyl)-quinoline oxidized.

These reactions are analogous to an earlier series carried out on thiophene by Gilman and Shirley.[5]



Experimental

Metalation of Thianaphthene.—An ethereal solution of *n*-butyllithium was prepared by the gradual addition with stirring of 295 g. (2.17 moles) of *n*-butyl bromide in 400 ml. of dry ether to 36.1 g. (5.35 moles) of lithium wire cut into 5–10 mm. lengths and suspended in 700 ml. of dry ether. The mixture was heated under reflux with continued stirring for one hour. A solution of 134 g. (1.00 mole) of thianaphthene in 300 ml. of dry ether was added, with stirring, to the filtered *n*-butyllithium solution and the mixture refluxed for 45 minutes.

Four-fifths of the resulting solution of 2-thianaphthenyllithium (I) was poured over a slurry of solid carbon dioxide and dry ether. After the evaporation of the carbon dioxide, 500 ml. of water was added, and the aqueous layer separated and acidified with concentrated hydrochloric acid. The precipitated solid was removed by filtration and recrystallized from dilute methanol, giving 77.5 g. (54.6% based on thianaphthene) of 2-thianaphthenecarboxylic acid melting at 236–236.5°. After a second recrystallization the acid melted at 237° and formed an amide which melted at 177°. Mayer[6] gives the melting point of thianaphthene-2-carboxylic acid (II) prepared by ring closure as 236° as do Schönberg, Petersen and Kaltschmidt[3] and Weissgerber and Kruber[2] who prepared the acid from 2-thianaphthenylsodium. The latter investigators proved the structure of the acid and prepared the amide, giving its melting point as 177°.

2-(2′-Thianaphthenyl)-quinoline (III).—To the remaining one-fifth of the 2-thianaphthenyllithium (I) solution, 25.8 g. (0.20 mole) of quinoline in 150 ml. of dry ether was added and the mixture stirred under reflux for one hour. The mixture was then hydrolyzed with 100 ml. of water and 20 ml. of nitrobenzene was added for the oxidation of the 1,2-dihydro-2-(2′-thianaphthenyl)-quinoline. After stirring for fifteen minutes the ethereal layer was separated, dried over anhydrous magnesium sulfate and distilled. The solid residue was recrystallized from ethyl alcohol and then from petroleum ether (b. p. 80–110°) to give 25.7 g. (49.4% based on thianaphthene) of yellow needles of 2-(2′-thianaphthenyl)-quinoline (III), m. p. 189.8–189.9° (cor.).

Anal. Calcd. for $C_{17}H_{11}NS$: N, 5.36. Found: N, 5.39.

A picrate prepared from ethereal solutions of picric acid and 2-(2′-thianaphthenyl)-quinoline melted at 221.5–222°.

(5) Gilman and Shirley, THIS JOURNAL, **71**, 1870 (1949).
(6) Mayer, *et al.*, *Ann.*, **488**, 259 (1931).

Anal. Calcd. for $C_{23}H_{14}N_4O_7S$: N, 11.5. Found: N, 11.8.

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Paper Chromatography of Anthraquinone Pigments

BY SHOJI SHIBATA, MICHIO TAKITO AND OSAMU TANAKA

The paper partition chromatography developed by Consden, Gordon and Martin[1,2,3] has been very usefully applied in the course of studies on the micro-determination of amino acids and carbohydrates. The separation of organic acids,[4] anthocyanins,[5] purines[6] and flavonoid pigments[7] has also been carried out by this method.

In the course of studies on the micro-determination of the principles of crude drugs, we have applied this method to the separation and identification of anthraquinone pigments.

In this preliminary report the procedures for separation, identification and determination of Rf-values of several synthetic and natural hydroxyanthraquinones are described. The relationship between the Rf-values and their structures is also discussed. We have found that benzine (b. p. 45–70°) saturated with 97% methyl alcohol is a very satisfactory solvent[8] for one-dimensional ascending separation of these compounds which are very sparingly soluble in water. The acetone solution of the mixture of authentic specimens of hydroxyanthraquinones spotted on a filter paper strip (2 cm. × 40 cm., Toyo-Filter Paper No. 2) was dried prior to the development. The development was carried out in a well closed glass cylinder (50 cm. in height and 12 cm. in diameter), for five to six hours at 24–25°, when the solvent ran about 30 cm. After air-drying, the developed paper strip was sprayed with 0.5% methyl alcoholic magnesium acetate solution and heated at 90° for five minutes. Distinct orange-red, purple or violet colored spots, depending on the position of hydroxyl groups in the anthraquinone nucleus, were given by this reagent.[9] Anthraquinones having at least one of the hydroxyl groups in the α-position develop with the reagent. Compounds which contain two in the 1,3-position, *i. e.*, emodin, chrysophanol or aloe-emodin, give an orange-red or pink color; those with two in the 1,4-position, *i.e.*, quinizarin, produce a purple; and those with two in the 1,2-position, *i.e.*, alizarin, exhibit a violet color.

This color reaction is specific, stable and very sensitive so that the very faint yellowish color on the paper strip given by a trace of hydroxyanthraquinone becomes clearly visible when the faint yellowish color is converted to a red or purple color by spraying with the magnesium

TABLE I

Rf-VALUES OF HYDROXYANTHRAQUINONES

(97% methyl alcohol saturated benzine as solvent, at 24–25°)

Subst.	Positions of substituents in anthraquinone nucleus	Rf[a]	Color of spot
Chrysophanol	4,5-Dihydroxy-2-methyl	0.92	Orange
Physcion	4,5-Dihydroxy-7-methoxy-2-methyl	.89	Orange
Quinizarin	1,4-Dihydroxy	.89	Purple
2-Methylquinizarin	1,4-Dihydroxy-2-methyl	.92	Purple
Emodin	4,5,7-Trihydroxy-2-methyl	.52	Pink
Rubiadin	1,3-Dihydroxy-2-methyl	.49	Orange-yellow
Aloe-emodin	4,5-Dihydroxy-2-hydroxymethyl	.15	Orange
Rhein	4,5-Dihydroxy-2-carboxyl	0	Orange
Alizarin	1,2-Dihydroxy	.04	Violet
Endocrocin	4,5,7-Trihydroxy-2-methyl-3-carboxyl	0	Pink
Purpurin	1,3,4-Trihydroxy	0.03	Purple
Dihydroxymethylanthraquinone	1,5-Dihydroxy-2-methyl	.92	Orange
	1,8-Dihydroxy-2-methyl	.92	Orange
Tetrahydroxyanthraquinone	1,3,5,7-Tetrahydroxy-2,6-dimethyl	.02	Orange
	1,3,6,8-Tetrahydroxy	.01	Orange-pink
Rhodocladonic acid	1,3,6,8-Tetrahydroxy-2-hydroxymethyl-7-carboxylic acid methyl ester	0	Orange
Anthragallol	1,2,3-Trihydroxy	0	Gray
Rufigallic acid	1,2,3,5,6,7-Hexahydroxy	0	Grayish-violet

[a] Rf values were measured to the leading edge of the spot.

(1) R. Consden, A. J. P. Martin and A. H. Gordon, *Biochemical J.*, **38**, 224 (1944).
(2) A. J. P. Martin, *Ann. New York Acad. Sci.*, **49**, 249 (1948).
(3) R. Consden, *Nature*, **162**, 359 (1948).
(4) B. T. Overell, *ibid.*, **160**, 87 (1947).
(5) E. C. Bate-Smith, *ibid.*, **161**, 835 (1948).
(6) E. Vischer and E. Chargaff, *J. Biol. Chem.*, **168**, 781 (1947).
(7) S. H. Wender and T. B. Gage, *Science*, **109**, 287 (1949).
(8) The temperature at which benzine is saturated with 97% methyl alcohol, which in this experiment was 19°, appears to have some effect on the Rf-values.
(9) S. Shibata, *J. Pharm. Soc. Japan*, **61**, 103 (in German) (1941).