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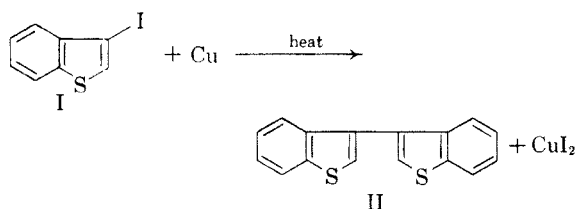
Preparation of 3-Arylthianaphthenes<sup>1,2</sup>ROBERT D. SCHUETZ AND LEON CIPORIN<sup>3</sup>

Received June 30, 1957

The synthesis of 3,3'-dithianaphthyl was accomplished by utilizing the Ullmann reaction with 3-iodothianaphthene. The preparation of 3-phenylthianaphthene and 3-(1'-naphthyl)thianaphthene was successfully realized by the reaction of 3-thianaphthylmagnesium bromide with the appropriate cyclic ketone followed by hydrolysis, dehydration, and dehydrogenation. Five previously unreported *o*-aroyl-*p*-chlorophenyl methyl sulfides were prepared by the Friedel-Crafts acylation of *p*-chlorophenyl methyl sulfide and the yields in the acylation reactions were correlated with the amount of steric hindrance involved in the formation of the sulfides. The ring closure, with chloroacetic acid, of three of the five *o*-aroyl-*p*-chlorophenyl methyl sulfides was carried out to yield the corresponding 5-chloro-3-aryl-2-thianaphthenecarboxylic acids which were previously unknown.

A study of restricted rotation in thianaphthene compounds containing an aryl group in the 3-position have recently been initiated in these laboratories. This paper is concerned with an investigation of the methods for the preparation of such compounds.

The symmetrical compound, 3,3'-dithianaphthyl (II) was prepared by the Ullmann procedure from 3-iodothianaphthene (I) and copper bronze. A small amount of a crystalline byproduct was isolated during the formation of 3,3'-dithianaphthyl (II) from 3-iodothianaphthene (I).

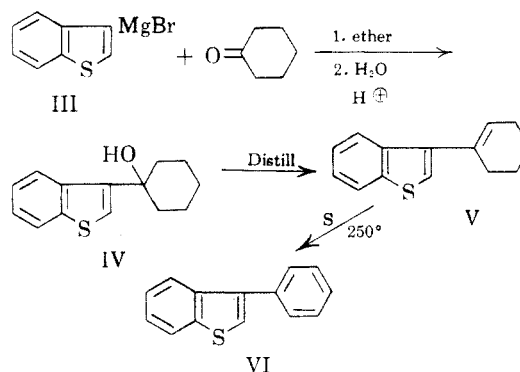


Although no structural studies were made on this substance, elementary analysis indicated that it is probably a polymer of thianaphthene. Steinkopf<sup>4</sup> has observed similar polymer formation when halothiophenes were submitted to the Ullmann reaction.

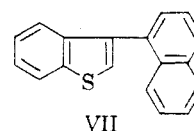
Attempts to effect the coupling of 3-thianaphthylmagnesium bromide (III) with metallic salts,<sup>5</sup> such as cupric chloride or nickel bromide, failed to yield 3,3'-dithianaphthyl (II).

The synthesis of 3-phenylthianaphthene (VI) was successfully accomplished by the reaction of 3-thianaphthylmagnesium bromide (III) with cy-

clohexanone followed by hydrolysis, dehydration, and dehydrogenation.



The same method, substituting  $\alpha$ -tetralone for cyclohexanone, was used in the synthesis of 3-(1'-naphthyl)thianaphthene (VII).



The 3-arylthianaphthenes, obtained for the first time, during the course of this work are summarized in Table I.

The three, previously unreported, 5-chloro-3-aryl-2-thianaphthenecarboxylic acids (XI) listed in Table II, were prepared from the appropriate *o*-aroyl-*p*-chlorophenyl methyl sulfide (IX) by treatment with chloroacetic acid. The sulfonium salt (X) has been proposed as an intermediate for this reaction by Krollpfeiffer and co-workers.<sup>6,7</sup>

The five, heretofore undescribed, *o*-aroyl-*p*-chlorophenyl methyl sulfides (IX) were prepared by the acylation of *p*-chlorophenyl methyl sulfide (VIII) with the appropriate aroyl chloride. An examination of the yields of the *o*-aroyl-*p*-chlorophenyl methyl sulfides (IX) reported in Table III confirms the observations of other investigators<sup>6,7</sup> concerning

(1) Abstracted from part of a dissertation submitted by Leon Ciporin to the Graduate School of Michigan State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented, in part, at the 130th meeting of the American Chemical Society, Atlantic City, N. J., Sept. 16-21, 1956.

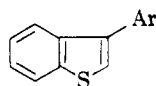
(3) Present address: E. I. du Pont de Nemours & Co., Inc., Greenville, N. C.

(4) W. Steinkopf, R. Leitsmann, and K. H. Hofmann, *Ann.*, **546**, 180 (1951).

(5) J. Krizewsky and E. E. Turner, *J. Chem. Soc.*, **115**, 559 (1919).

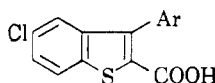
(6) F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Ann.*, **563**, 15 (1949).

(7) F. Krollpfeiffer, K. L. Schnider, and W. Wissner, *Ann.*, **566**, 139 (1950).

TABLE I  
 3-ARYLTHIANAPHTHENES<sup>a</sup>


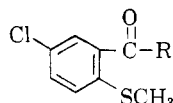
Ar	Formula	M.P., °C.	Yield, %	Analyses			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
Phenyl	C <sub>14</sub> H <sub>10</sub> S	172-173	17	79.9	79.3	4.8	4.9
1'-Naphthyl	C <sub>18</sub> H <sub>12</sub> S	90-92	38	83.0	82.8	4.7	4.9
3'-Thianaphthyl	C <sub>15</sub> H <sub>10</sub> S <sub>2</sub>	>370	56	72.1	71.9	3.8	3.5

<sup>a</sup> All melting points are uncorrected.

 TABLE II  
 5-CHLORO-3-ARYL-2-THIANAPHTHENECARBOXYLIC ACIDS


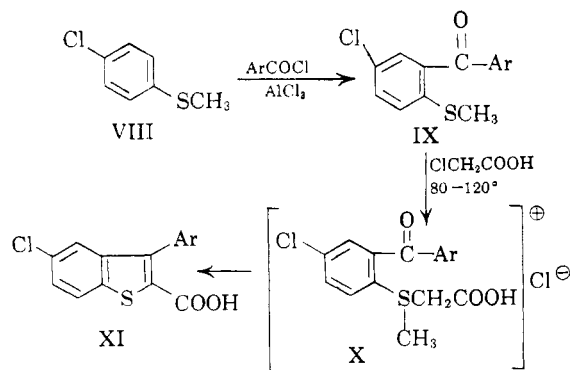
Ar	Formula	M.P., °C. <sup>a</sup>	Yield, %	Analyses					
				Neut. Equiv.		Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl	C <sub>15</sub> H <sub>9</sub> ClO <sub>2</sub> S	263-265	16	288	287	62.4	62.2	3.1	3.4
α-Thienyl	C <sub>13</sub> H <sub>5</sub> ClO <sub>2</sub> S <sub>2</sub>	267-268	53	294	292	52.9	52.7	2.4	2.9
<i>o</i> -Carboxyphenyl <sup>b</sup>	C <sub>15</sub> H <sub>12</sub> ClO <sub>4</sub> S	282-284	61	179	177	60.3	60.2	3.1	3.3

<sup>a</sup> These compounds decompose at their melting points. <sup>b</sup> Analysis is for a compound with one-third mole of benzene of crystallization.

 TABLE III  
*o*-AROYL-*p*-CHLOROPHENYL METHYL SULFIDES


R	Formula	M.P., °C.	Yield, %	Analyses			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
Phenyl	C <sub>14</sub> H <sub>12</sub> ClOS	101-103	38	64.0	64.1	4.2	4.1
α-Naphthyl	C <sub>18</sub> H <sub>14</sub> ClOS	115-117	4	69.1	68.5	4.2	3.9
β-Naphthyl	C <sub>18</sub> H <sub>14</sub> ClOS	120-121	25	69.1	68.6	4.2	4.0
α-Thienyl <sup>a</sup>	C <sub>17</sub> H <sub>9</sub> ClOS <sub>2</sub>	77-78	35	51.9	51.9	2.8	2.7
<i>o</i> -Carboxyphenyl	C <sub>15</sub> H <sub>13</sub> ClO <sub>3</sub> S	183-185	13	58.7	58.7	3.6	3.8

<sup>a</sup> Isolated as the thiophenol rather than as the methyl sulfide.



the steric hindrance offered by a thiomethyl group to acylation in the ortho position with respect to

such a group in the benzene series. The acyl groups, listed in order of decreasing yield of the sulfides are,

benzoyl ≥ α-thenoyl > β-naphthyl >

*o*-carboxybenzoyl > α-naphthoyl

This is the order to be expected on the basis of increasing steric hindrance, due to the size of the attacking carbonium or potential carbonium ion in the acylation reaction.

In the Friedel-Crafts acylation of *p*-chlorophenyl methyl sulfide with 2-thenoyl chloride, cleavage of the thioether occurred and *o*-(2-thenoyl)-*p*-chlorothiophenol was obtained as the product of the acylation reaction. There is ample precedent for the cleavage of a thioether with anhydrous aluminum

chloride. Alkyl aryl ethers are dealkylated by warming with aluminum chloride to yield the free phenol.<sup>8</sup> However, we are unable to explain the absence of thioether cleavage in the acylations carried out with acylhalides other than 2-thenoyl chloride.

All attempts to effect the ring closure of *o*-(1-naphthoyl)-*p*-chlorophenyl methyl sulfide or its 2-naphthoyl isomer failed. Instead, ketonic cleavage occurred yielding  $\alpha$ -naphthoic and  $\beta$ -naphthoic acids from the 1-naphthoyl and 2-naphthoyl isomers, respectively, as the only isolable products. The sulfide, *o*-benzoyl-*p*-chlorophenyl methyl sulfide, which did yield a ring closure product, also underwent some ketonic cleavage to yield benzoic acid.

#### EXPERIMENTAL

*3,3'-Dithianaphthyl.* 3-Iodothianaphthene was prepared from thianaphthene and iodine according to the method of Gaertner.<sup>9</sup> Commercial copper bronze was activated by the method of Kleiderer and Adams<sup>10</sup> immediately prior to its use.

3-Iodothianaphthene, 0.50 g. (0.019 mole), was placed in a Pyrex test tube and heated to 150° in an oil bath. As the temperature was gradually raised to 270° over a period of 20 min., 2.5 g. (0.039 mole) of copper bronze was added in small portions to the reaction mixture while stirring it with a thermometer. After the addition of the copper bronze was complete, the temperature was maintained in the range 270–280° for 2 hr. The cooled reaction mass was extracted with two 25-ml. portions of cold chloroform and on evaporation of the solvent 0.2 g. of a light tan polymeric substance was obtained which melted at 258–259°, after two recrystallizations from benzene.

*Anal.* Calcd. for  $(C_8H_6S)_x$ : C, 71.6; H, 4.5. Found: C, 71.0; H, 4.4.

The residue from the chloroform extraction was placed in a Bailey-Walker type extractor and extracted with 30 ml. of hot chloroform for 2 hr. Filtration of the cooled solution yielded 0.4 g. (0.0015 mole; 17%) of crude 3,3'-dithianaphthyl melting above 370°. The analytical sample was recrystallized from benzene.

*3-Arylthianaphthenes.* 3-(1'-Cyclohexenyl)thianaphthene and 3-(3',4'-dihydro-1'-naphthyl)thianaphthene were prepared by the method of Szmuskovicz and Modest.<sup>11</sup> Aromatization of the cycloalkenylthianaphthenes was accomplished by the following procedure. An intimate mixture of the compound and the required quantity of powdered sulfur was heated in an oil bath maintained in the temperature range 240–250° until hydrogen sulfide evolution ceased.

(8) C. Hartmann and L. Gotterman, *Ber.*, **25**, 3531 (1892).

(9) R. Gaertner, *J. Am. Chem. Soc.*, **74**, 4950 (1952).

(10) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4219 (1933).

(11) J. Szmuskovicz and E. J. Modest, *J. Am. Chem. Soc.*, **72**, 571 (1950).

The cooled reaction mass was dissolved in hot benzene and the unreacted sulfur was removed by filtration. The cooled filtrate was washed with 10% aqueous sodium sulfite and dried in contact with anhydrous sodium sulfate. After evaporating the benzene, the solid residue was sublimed in the temperature range of 230–240° under a pressure of 10 mm. The crystalline product was recrystallized from 95% ethanol.

*p*-Chlorophenyl methyl sulfide. A 100 g. (0.69 mole) quantity of *p*-chlorothiophenol was dissolved in 350 ml. of 10% aqueous sodium hydroxide. While stirring the alkaline solution, 177 g. (1.40 mole) of dimethyl sulfate were added dropwise over a 0.5-hr. period. During the course of the reaction, an additional 150 ml. of 10% aqueous sodium hydroxide were added to the reaction mixture to maintain its alkalinity. The oily product was extracted with ether, dried, and the ether was evaporated. Distillation of the residue yielded 94.7 g. (0.60 mole; 87%) of a product; b.p. 107° (14 mm.),  $n_D^{20}$  1.5997. The reported<sup>12</sup> b.p. is 170° (760 mm.) for *p*-chlorophenyl methyl sulfide.

*o*-Aroyl-*p*-chlorophenyl methyl sulfides. Equimolar quantities of the aroyl chloride and anhydrous aluminum chloride were brought to a temperature approximately 5° above the melting point of the aroyl chloride by immersion of the mixture in an oil bath. Then, one-sixth to one-third of the required quantity of *p*-chlorophenyl methyl sulfide was added dropwise, during 0.5 hr., to the reaction mixture which was held at the original temperature for 10 hr. after the addition of the aroyl chloride was complete. The cooled reaction complex was poured into a slurry of dilute hydrochloric acid and crushed ice and extracted with ether. The ether extract was washed with 10% aqueous sodium hydroxide and dried in contact with anhydrous magnesium sulfate. After removing the drying agent by filtration and evaporating the ether, the residue was distilled.

*o*-(2-Carboxyphenyl)-*p*-chlorophenyl methyl sulfide. A mixture of 10 g. (0.062 mole) of *p*-chlorophenyl methyl sulfide, 4.6 g. (0.031 mole) of phthalic anhydride, and 10.5 g. (0.065 mole) of anhydrous aluminum chloride was maintained at a temperature of 80° for 4 hr. The reaction mixture was cooled, decomposed with water, and steam distilled to remove the unreacted *p*-chlorophenyl methyl sulfide. The residual solid was collected by filtration and extracted with hot chloroform in which the unreacted phthalic anhydride is insoluble. After evaporating the chloroform, the solid residue was washed with petroleum ether and recrystallized from aqueous acetic acid.

*Anal.* Calcd. for  $C_{15}H_{13}ClO_3S$ : *Neut. equiv.* 307. Found: 302.

*5-Chloro-3-aryl-2-thianaphthencarboxylic acids.* The *o*-aroyl-*p*-chlorophenyl methyl sulfide was added to a four to six mole excess of chloroacetic acid. The resulting solution was kept in the temperature range of 80–130°, for periods of time varying from 10 to 72 hr. The addition of water to the cooled reaction solution precipitated the thianaphthencarboxylic acid which was collected and recrystallized from benzene.

EAST LANSING, MICH.

(12) K. Brand and W. Groebe, *J. prakt. Chem.*, **108**, 1 (1924).