Experiments in the Synthesis of 3,4-Benzo-9-Thiafluorene, a Sulfur Analog of 3,4-Benzophenanthrene.

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EXPERIMENTS IN THE SYNTHESIS OF 3,4-BENZO-9-THIAFLUORENE, A SULFUR ANALOG OF 3,4-BENZOPHENANTHRENE

by

Clifton Rems Neumoyer

A DISSERTATION
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

Lehigh University
1944

This dissertation is accepted and approved in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Professor in Charge

E D Amstutz

Special Committee directing the doctoral work of Clifton Rems Neumoyer.

A C Zettlemoyer
H A Neidig
E D Amstutz
C C Bidwell.

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INTRODUCTION

It has been recognized since the time of Victor Meyer's classical experiments on thiophene that a sulfur atom substituted for a vinylene group of an aromatic carbocycle may cause little change in the physical and chemical properties of the compounds (16). Table I, taken from Meyer and Jacobsen, "Lehrbuch der Organischen Chemie," Vol. 2, Part 3, p. 121, shows that both the melting points and the boiling points of many thiophene derivatives do not differ widely from those of the corresponding carbocyclic derivatives. On passing to the condensed polynuclear systems, it is readily seen from Table II that the two systems do not show the same relationship between their respective melting points; however, it must be remembered that melting point correlations are generally not as consistent as those of boiling points.

In addition to the physical and chemical properties of an aromatic carbocycle being similar to those of the sulfur analog, it is often found that biological effects of the corresponding members of both series are similar also. One of the recent correlations of this kind was made by Sandin and Fieser (18). It was found (5) that 4,9-dimethyl-5,6-benzothiophanthrene exhibited carcinogenic properties similar to one of the corresponding carbocyclic substances, 9,10-dimethyl-1,2-benzanthracene.

Three series of experiments designed to produce the 3,4-benzo-9-thiafluorene nucleus and one of its methyl derivatives are reported in this thesis. The ring system is angular and is to be related to 3,4-benzophenanthrene. The isomer 2,3-benzo-9-thiafluorene is linear and is one of the sulfur isologs of the angular hydrocarbon 1,2-benzanthracene. While the

Table I

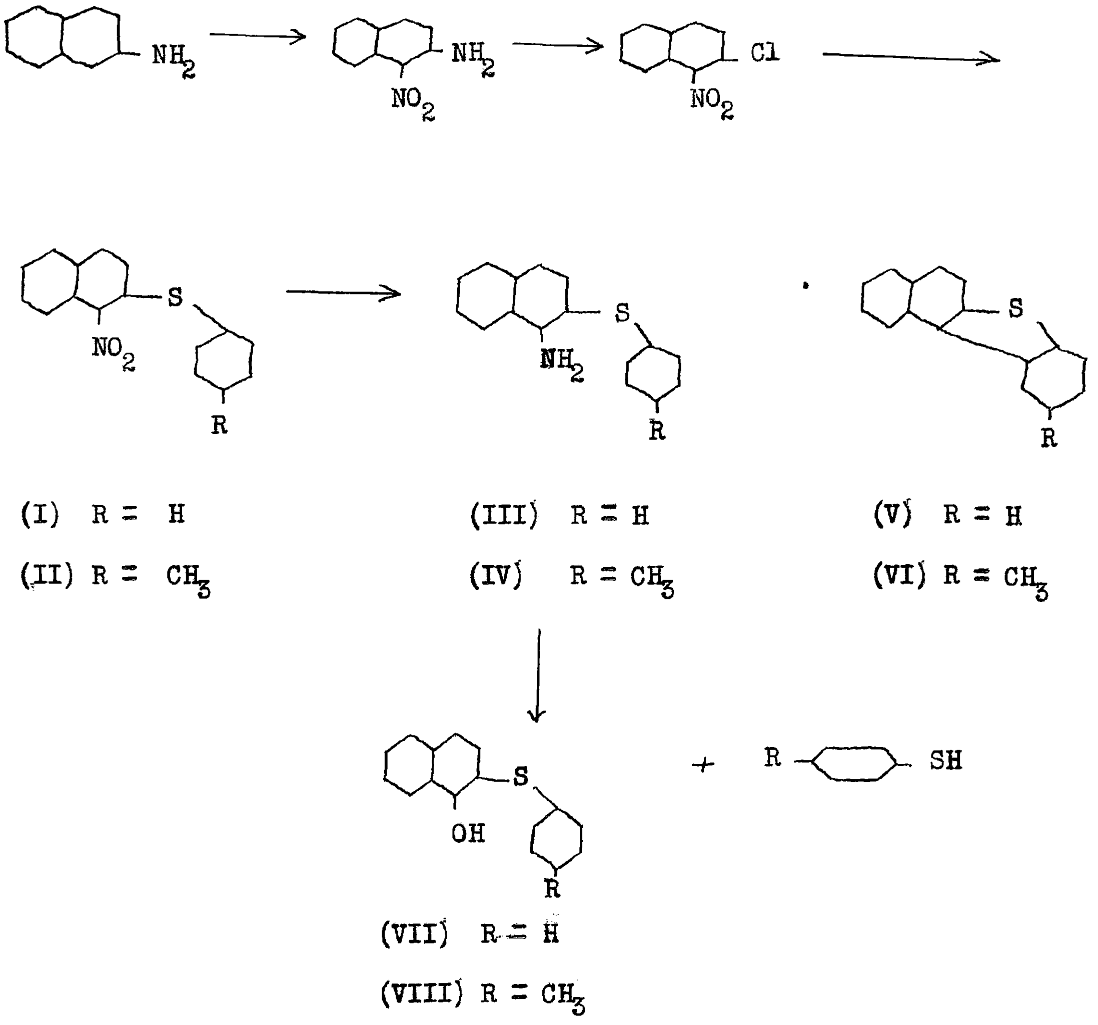
Name of Thiophene Derivative	Boiling Points of Derivatives in °C	
	Thiophene	Benzene
2-Methyl thiophene	112-113	111
3-Methyl thiophene	114	111
2-Ethyl thiophene	132-134	135
2,3-Dimethyl thiophene	136-137	143
3,4-Dimethyl thiophene	144-146	143
2,4-Dimethyl thiophene	137-138	139
2,5-Dimethyl thiophene	134 (730 mm.)	137
Tetramethyl thiophene	182-184 (uncorr.)	204
2-Bromo thiophene	149-151 (uncorr.)	157
Tetrabromo thiophene	326	329
2-Iodo thiophene	182 (uncorr.)	189
2-Nitro thiophene	224-225	209
2-Amino thiophene	77-79 (11 mm.)	71 (9 mm.)
α-Thienyl alcohol	207	205
α-Thiophene aldehyde	192	179
α-Aceto thiophene	213.5	202
α-Thiophenic acid	260 126.2 (m.p.)	249 121 (m.p.)
β-Thiophenic acid	138.4 (m.p.)	121 (m.p.)
α-Thiophene acid amide	173-175 (m.p.)	128 (m.p.)
β-Thiophene acid amide	178 (m.p.)	128 (m.p.)
α,α-Dithienyl	260 (uncorr.)	254
Di-α-thienyl ketone	326 (uncorr.)	306
Triphenyl thienyl methane	433-438	431

Table II

Name of Heterocycle	Melting Point (°C)	Name of Corresponding Carbocycle	Melting Point (°C)
Thiophene	- 40	Benzene	5.5
Benzothiophene	31	Naphthalene	80.2
4,5 - Benzothionaphthene	108	Phenanthrene	99-100
Dibenzothiophene	97	"	99-100
3,4 - Benzo-9-thiafluorene	174.2-175.7 (?)	3,4-Benzo-phenanthrene	158-160
Benzothiophanthrene	154-155	1,2-Benzanthracene	141
Dinaphtho (2,1,1',2')-thiophene	202	3,4,5,6-Dibenzo-phenanthrene	145-146

2,3-benzo-9-thiafluorene series is well known, a search of the literature reveals the fact that no member of the 3,4-benzo-9-thiafluorene series has yet been prepared. Interest in this series of compounds therefore concerns not only the possible carcinogenic activity of the substances but also the chemistry of their formation and reactions.

DISCUSSION



(I) R = H

(II) R = CH_3

(III) R = H

(IV) R = CH_3

(V) R = H

(VI) R = CH_3

(VII) R = H

(VIII) R = CH_3

This method of synthesis seemed to be especially desirable since it eliminates the possibility of the formation of isomers.

The condensation (4) of 1-nitro-2-chloronaphthalene with thiophenol or with p-thiocresol was carried out in good yield. In order to ascertain that no rearrangement took place during condensation (8,9), an authentic sample of p-tolyl 4-nitro-1-naphthyl sulfide was prepared and by the method of mixed melting points, it was found that this compound and the compound prepared from 1-nitro-2-chloronaphthalene and p-thiocresol were not identical.

The reduction of phenyl 1-nitro-2-naphthyl sulfide and the corresponding p-tolyl compound was attempted by various methods but that using stannous chloride-hydrogen chloride in acetic acid solution (3) is to be preferred not only because of its good yield but also because of the ease of purification of the resulting amine. During the course of the reduction some splitting of the sulfide must have taken place since in each case there was a pronounced odor of the corresponding thiophenol.

The ring-closure reaction (4) (a modification of Pschorr's process) was carried out by diazotization of the amine with subsequent refluxing in 50% sulfuric acid solution. One of the products isolated in minute amount was the disulfide of the corresponding thiophenol which must have been produced during the diazotization or the refluxing since the amines used in this reaction had been purified through their hydrochlorides and could therefore be assumed to be free of the thiophenol. The disulfide collected in the condenser and in the case of the phenyl compound the diphenyl disulfide was identified by a mixed melting point determination with an authentic sample made by oxidation of an alcoholic ammonia solution of thiophenol. Most of the product was obtained as a black tar which solidified on cooling and was very soluble in ether, benzene and acetic acid. This tarry mixture was separated by extraction with ligroin followed by chromatography of the ligroin solution over Brockmann alumina. The resulting chromatogram was developed with a 50% (by vol.) solution of ligroin in benzene after which each band was extracted with ether.

The two uppermost bands contained the dark colored impurities which were not further investigated. The third band contained the corresponding phenyl and p-tolyl 1-hydroxy-2-naphthyl sulfide, the former being obtained in 1% yield and the latter in 6.5% yield. In both cases the lowest band contained a pale yellow compound which was insoluble in Claisen's alkali. The compound from phenyl 1-amino-2-naphthyl sulfide after twice repeated recrystallization from about 75% aqueous acetic acid melted at 174.2 - 175.7° and was obtained in 0.4% yield. Since repeated recrystallization resulted in considerable loss, further purification of the compound was attempted by rechromatography over alumina. This operation yielded only an unrecrystallizable oil. Vacuum sublimation lowered the melting point and did not improve the melting range (170.1 - 172.2°). The substance from p-tolyl 1-amino-2-naphthyl sulfide melted at 221.4 - 225.4° and was obtained in only minute amount. Neither compound was found to exhibit pro-oxidant properties on lard (14). The analysis of the phenyl compound for sulfur did not check the calculated value. The phenyl compound was oxidized with hydrogen peroxide in glacial acetic acid solution on the water bath and the analysis of this product likewise did not check the sulfur value calculated for the sulfone, both analyses being low by a fairly constant amount.

It is interesting to note that the melting point of the compound from phenyl 1-amino-2-naphthyl sulfide falls on a practically straight line obtained by plotting melting point vs. molecular weight for the following compounds : thiophene (mol. wt. 84; m.p. -37°), benzothiophene (mol. wt. 134; m.p. 31°) and 4,5-benzothionaphthene (mol. wt. 184; m.p. 108 - 109°). Figures I to IV show the melting point - molecular weight relationships of some of the heterocyclic and some of the carbocyclic compounds.

The neutral substances isolated from the lowest bands of the chromatograms cannot be the sulfides formed by replacement of the diazonium groups by H since those compounds are known to be distinctly different. Phenyl 2-naphthyl sulfide melts at 51.8° (2) and p-tolyl 2-naphthyl sulfide melts at 70.5° (1). Moreover, both are colorless. It is possible that the products represent mixtures of the desired compounds with impurities low in sulfur but the matter cannot be settled definitely from the available data.

The ring-closure reaction was also found to give very inconsistent results; a total of 39.8 g. of phenyl 1-amino-2-naphthyl sulfide yielded 235.5 mg. of the supposed 3,4-benzo-9-thiafluorene, of which 232.5 mg. were obtained in one reaction starting with 12.9 g. of amino compound.

Attempts to carry out the ring-closure reaction by several other modifications (11,17) were unsuccessful.

It was concluded that the poor and inconsistent yields from the various modifications of the Pschorr synthesis might possibly be due to failure of the diazotization step. Since good yields are usually obtained in a Sandmeyer reaction, it was decided to prepare phenyl 1-chloro- and phenyl 1-bromo-2-naphthyl sulfide from the corresponding amine by this reaction (10). It seems logical that the yield in the ring-closure could not be expected to be better than that in the Sandmeyer. The chloro-compound was obtained in 12.5% yield and the bromo-compound in 8.7% yield. In each case an appreciable amount of an amine was recovered by treatment of the ether solution of the product with dry hydrogen chloride.

Having obtained the two halogeno-compounds, a ring-closure reaction on

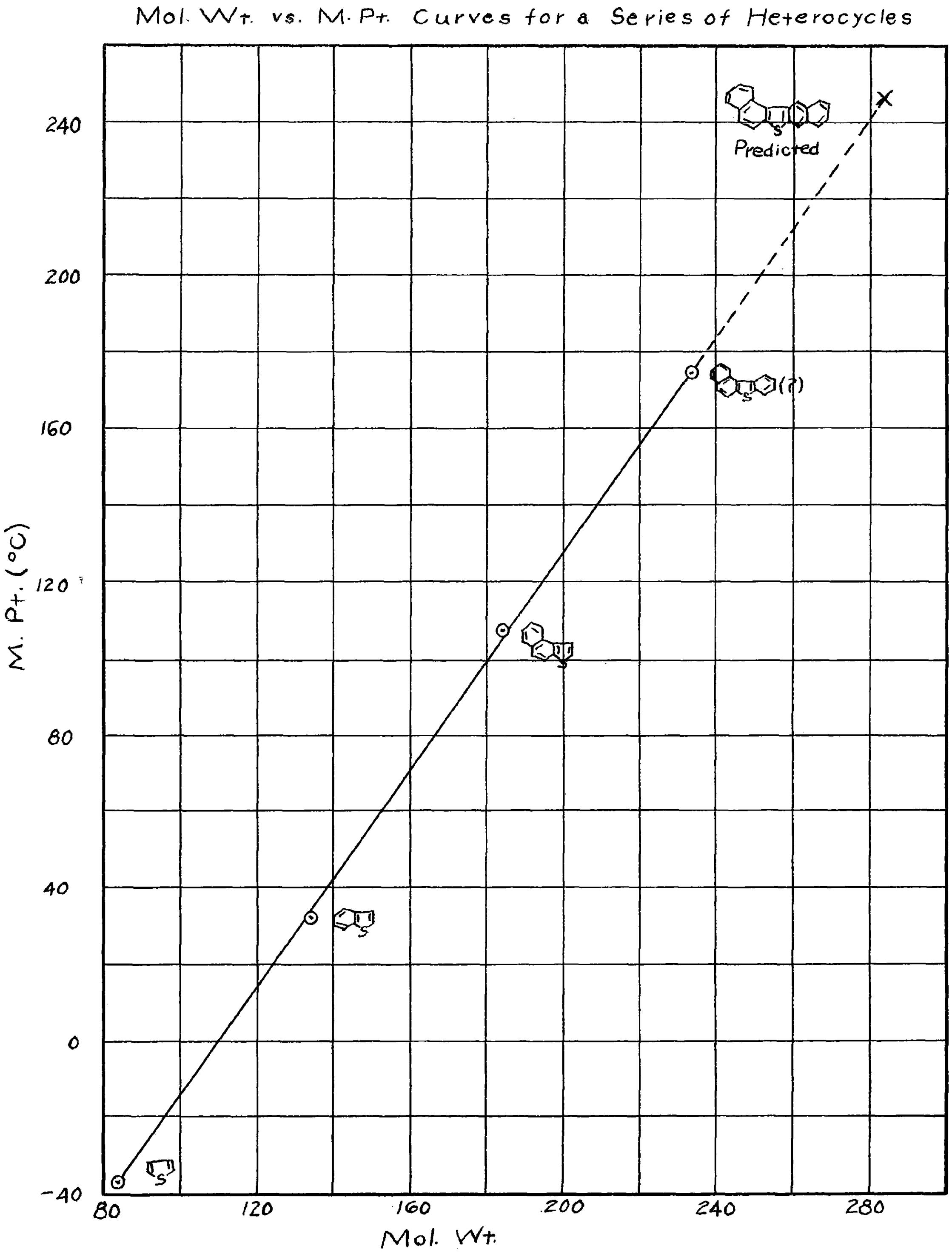

Mol. Wt. vs. M.Pt. Curves for a Series of Heterocycles
M. Pt. (°C)
240
200
160
120
80
40
0
-40
80
120
160
200
240
280
Mol. Wt.
Predicted
(?)
S

Figure I

Log Mol. Wt. vs. Log M. Pt. Curves for a Series of Heterocycles

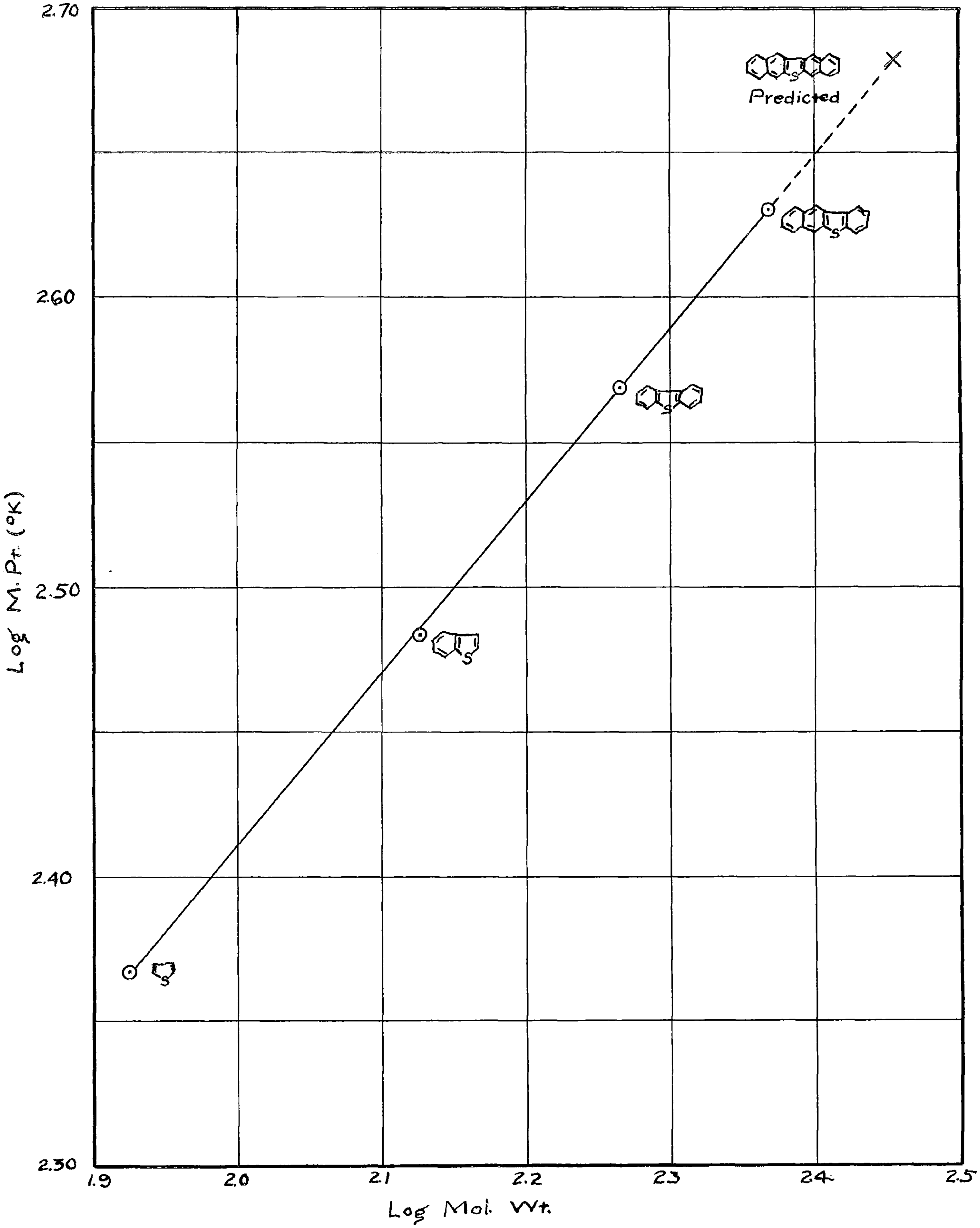


Figure II

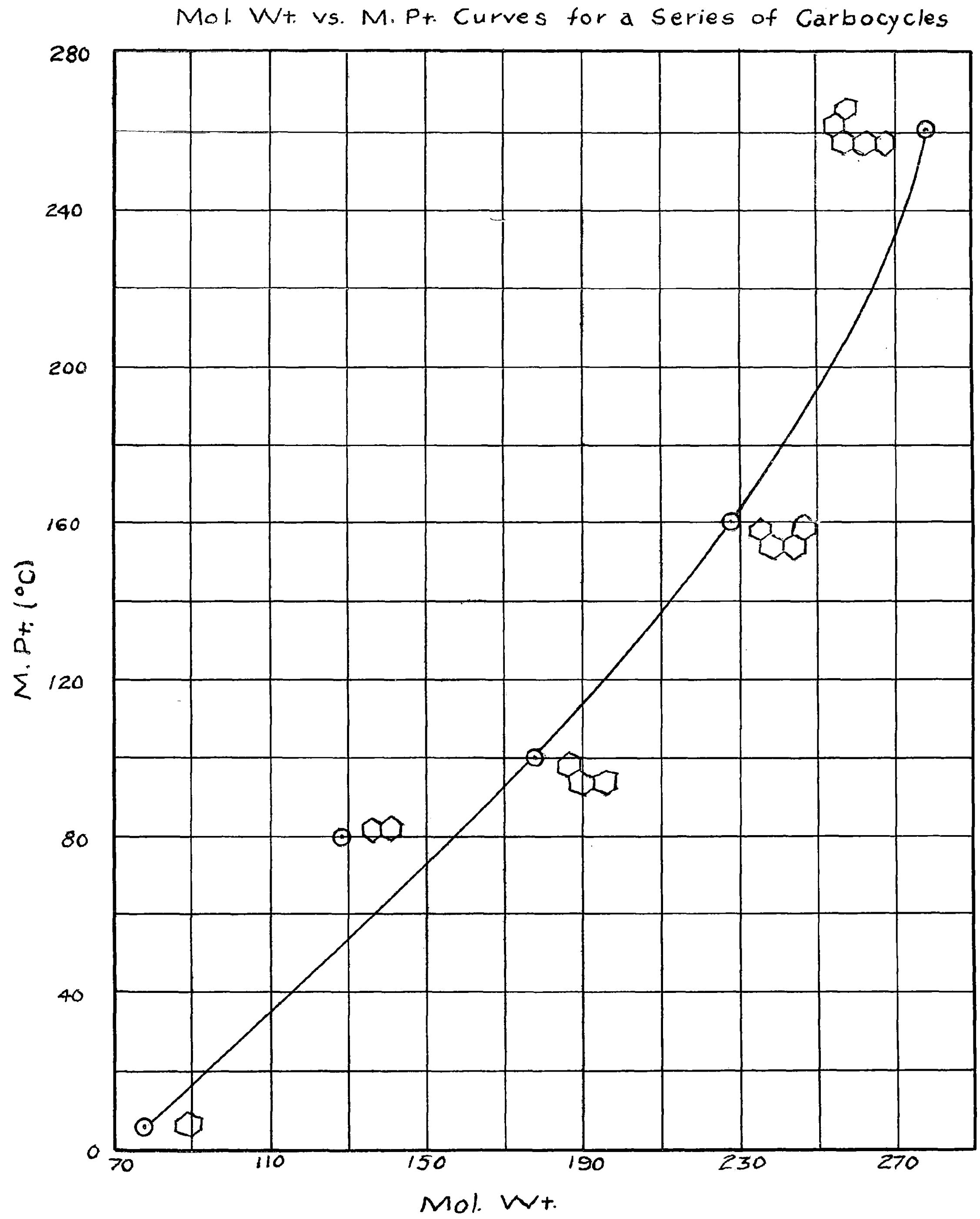

Mol. Wt. vs. M. Pt. Curves for a Series of Carbocycles
M. Pt. (°C)
280
240
200
160
120
80
40
0
70
110
150
190
230
270
Mol. Wt.

Figure III

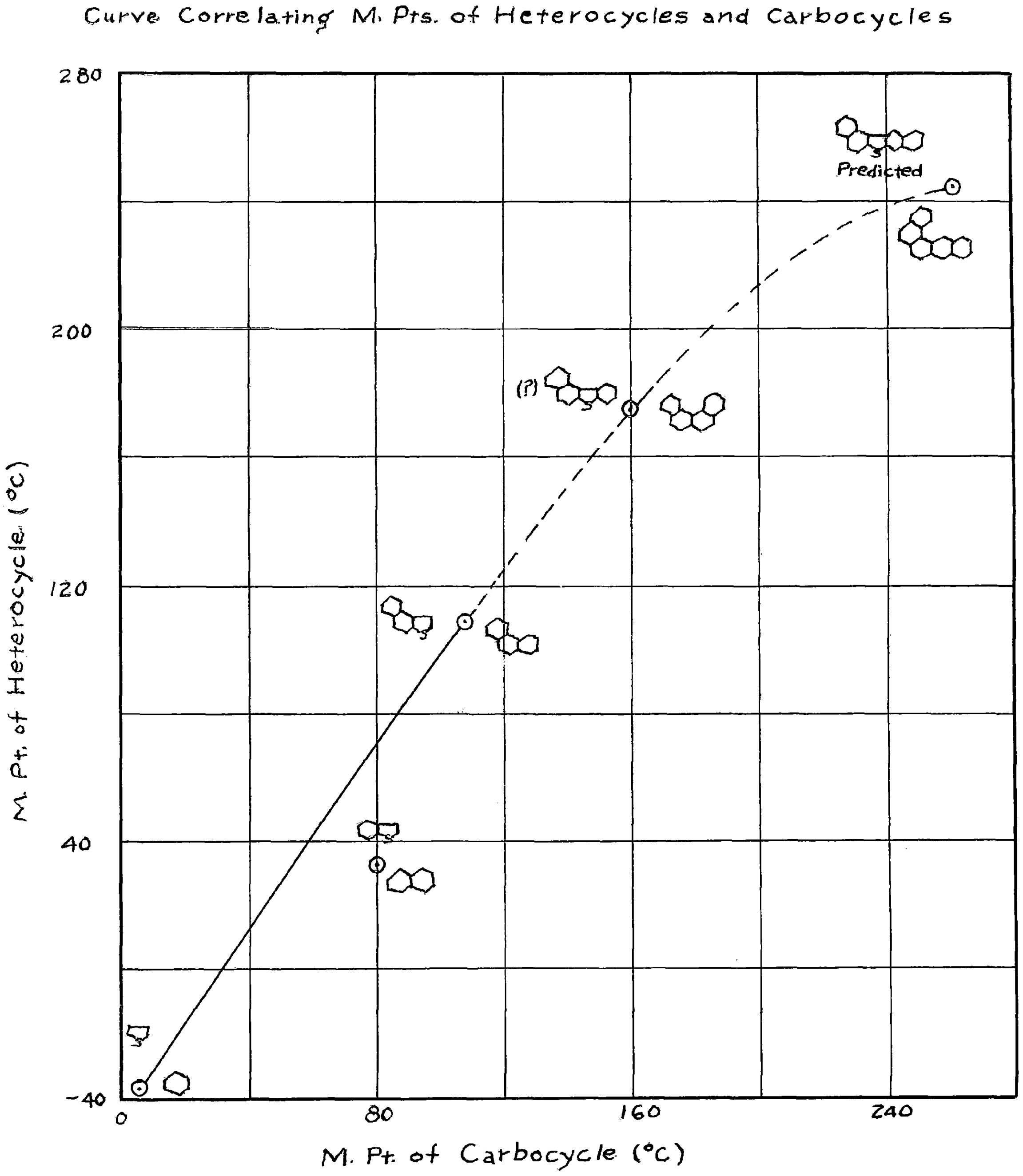
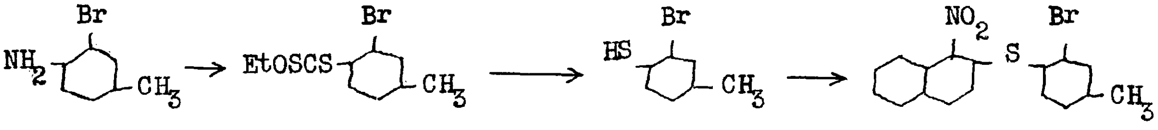

Curve Correlating M. Pts. of Heterocycles and Carbocycles
280
200
120
40
-40
0
80
160
240
M. Pt. of Carbocycle (°C)
M. Pt. of Heterocycle (°C)
Predicted
(?)
S

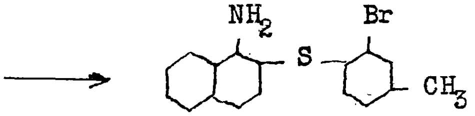
Figure IV

each was attempted with anhydrous aluminum chloride in carbon disulfide solution. The chloro-compound was recovered unchanged and the bromo-compound yielded a tar which on chromatographic adsorption produced an oil that could not be made to crystallize.

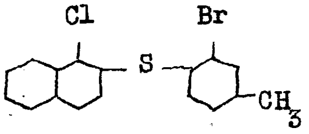
A third method which seemed to be of possible value was a modified Ullmann reaction on o-bromo-p-tolyl 1-chloro-2-naphthyl sulfide (from 1-nitro-2-chloronaphthalene and 2-bromo-4-methylthiophenol) since this also eliminates the possibility of the formation of isomers.



(IX)



(X)



(XI)

o-Bromo-p-tolyl 1-nitro- and o-bromo-p-tolyl 1-amino-2-naphthyl sulfide were obtained in good yields by reactions analogous to those for(II) and (IV), respectively. A Sandmeyer reaction on the amino-compound gave no product which could be identified as the dihalogen compound (XI).

The poor yields of supposed ring-closed compound from the modified Pschorr synthesis are in accord with the anomalous reactions of the amino-compound in the Sandmeyer reaction. The amine is relatively unstable, oxidizing easily in air and undergoing gradual change on storage under usual laboratory conditions. The poor yields obtained in the Sandmeyer reaction and the isolation of a considerable quantity of amino-compound, which analysed correctly for phenyl 1-amino-2-naphthyl sulfoxide, is also added evidence for the anomalous reaction of the corresponding amino-sulfide. In the ring-closure reactions of both phenyl and p-tolyl compounds, the yield of hydroxy-sulfides greatly exceeded that of the desired substances, indicating hydrolysis of the diazonium compounds. These reactions plus the fact that the diphenyl disulfide and the corresponding p-tolyl disulfide were isolated indicates that the Pschorr reaction is only one of perhaps many competing reactions.

EXPERIMENTAL

The corrected melting points have been recorded in all cases and were determined in a Thiele melting point tube.

Phenyl 1-nitro-2-naphthyl sulfide (I).--- 1-Nitro-2-aminonaphthalene (19) was prepared in an overall yield of 51.3% (cf. Table III). After recrystallization from alcohol, it melted at 125.1 - 127.1°. This was converted into 1-nitro-2-chloronaphthalene (10), 28.2 g. (0.15 mol.) of 1-nitro-2-aminonaphthalene yielding 20.2 g. of the compound which melted at 98.7 - 100.2°, (lit. (7), m.p. 99 - 100°) after recrystallization from alcohol (cf. Table IV). Using an adaptation of the method of Cullinane, et al (4), 21.1 g. (0.102 mol) of 1-nitro 2-chloronaphthalene and 13.7 g. (0.125 mol) of thiophenol were dissolved in 139 ml. of hot alcohol and a concentrated aqueous solution of 7.0 g. (0.130 mol) of potassium hydroxide added after which the solution was refluxed twelve hours in an atmosphere of nitrogen. After cooling in a refrigerator over night, the precipitate was filtered off and washed successively with water, dilute aqueous sodium hydroxide solution and water. The crude product weighed 28.4 g. (99% of theory) and after recrystallization from 222 g. of alcohol containing Darco, the brilliant yellow compound weighed 24.6 g. (85% of theory) and melted at 58.5 - 59.5°(lit. (8), m.p. 58-58.5°); cf. Table V.

Table III

Preparation of 1-Nitro-2-aminonaphthalene

Run No.	Wt. of β-Naphthylamine (g.)	Wt. of 1-Nitro-2-aminonaphthalene (g.)	% Yield
1	123	94.8	59.0
2	141	82.7	44.5
3	200	108.2	41.0
4	174	118.0	51.5
5	200	136.3	52.0

Table IV

Preparation of 1-Nitro-2-chloronaphthalene from 1-Nitro-2-aminonaphthalene

Run No.	Wt. of 1-Nitro-2-aminonaphthalene (g.)	Wt. of 1-Nitro-2-chloronaphthalene (g.)	% Yield
1	28.2	20.2	65.0
2	28.2	23.5	75.5
3	28.2	27.1	87.0
4	11.0	9.7	79.5
5	28.2	19.3	62.0
6	94.6	76.0	72.5
7	28.2	17.9	57.5
8	64.5	18.9	26.5
9	28.2	16.5	53.0
10	28.2	16.2	52.0
11	28.2	20.0	64.0

Table V

Reaction of 1-Nitro-2-chloronaphthalene with Thiophenol

Run No.	Wt. of 1-Nitro-2-Chloronaphthalene (g.)	Wt. of Thiophenol (g.)	Wt. of Phenyl 1-nitro-2-naphthyl sulfide(g.)	% Yield
1	16.2	10.4	19.2	87.5
2	18.9	12.2	24.4	95.5
3	21.1	13.7	28.4	99.5
4	16.5	10.7	21.1	94.5

Phenyl 1-nitro-2-naphthyl sulfoxide was prepared in 71% yield from the corresponding sulfide by oxidation with a 30% solution of hydrogen peroxide (10% excess) in glacial acetic acid solution at room temperature. The compound melted at 80.5 - 82.0° after recrystallizing twice from alcohol. An attempted reduction of this compound to phenyl 1-amino-2-naphthyl sulfoxide by the stannous chloride- hydrogen chloride method yielded a tar which could not be made to crystallize.

Anal. Calcd. for $C_{16}H_{11}O_3NS$: S,10.78. Found: S,10.54.

Phenyl 1-nitro-2-naphthyl sulfone was also prepared from the corresponding sulfide in quantitative yield by oxidation with an excess of hydrogen peroxide in glacial acetic acid solution at the temperature of the boiling water bath. After recrystallization from glacial acetic acid, the compound melted at 147.8 - 149.2°.

Anal. Calcd. for $C_{16}H_{11}O_4NS$: S,10.23. Found: S,10.34.

<u>p-Tolyl 1-nitro-2-naphthyl sulfide (II).</u>-This compound was obtained in 85% yield in a manner similar to that for (I) except that the reaction

mixture was filtered hot immediately after refluxing (cf. Table VI). After recrystallization from alcohol containing Darco, the brilliant yellow compound melted at 105.2 - 105.9°.

Anal. Calcd. for $C_{17}H_{13}O_2NS$: N,4.74. Found: N,4.85, 5.11, 4.87.

Table VI

Reaction of 1-Nitro-2-chloronaphthalene with p-Thiocresol

Run No.	Wt. of 1-Nitro-2-chloronaphthalene (g.)	Wt. of p-Thiocresol (g.)	Wt. of p-Tolyl 1-nitro-2-naphthyl sulfide (g.)	% Yield
1	16.2	10.8	19.5	85.0
2	11.5	7.7	12.5	77.0
3	18.5	12.4	20.8	79.5
4	16.2	10.8	19.2	83.5
5	49.2	32.8	58.9	84.5

p-Tolyl 1-nitro-4-naphthyl sulfide, prepared as above from 4-chloro-1-nitronaphthalene and p-thiocresol, was obtained as a red crystalline compound melting at 108.2 - 110.0° after recrystallization from alcohol. A mixture of this compound with (II) melted at 79 - 90°.

Anal. Calcd. for $C_{17}H_{13}O_2NS$: S, 10.86. Found: S, 11.14.

Phenyl 1-amino-2-naphthyl sulfide (III).-A mixture of 54 g. of stannous chloride in 146 ml. of glacial acetic acid was treated with dry hydrogen chloride until a clear solution was obtained. This solution was then added to a solution of 20g. of (I) in 80 ml. of glacial acetic acid at 80°. After stirring at this temperature for one hour, the reaction mixture was poured into water and extracted with ether. The ether solution was washed with water and a saturated sodium bicarbonate solution and then dried over anhydrous magnesium sulfate after which the hydrochloride of (III) was precipitated by treatment with dry hydrogen chloride. After filtration, the precipitate was washed as rapidly as possible with dry ether (the hydrochloride being unstable in the presence of moisture) and then treated with a saturated sodium bicarbonate solution. The free amine was extracted with ether and the ether extract dried over anhydrous magnesium sulfate. Evaporation of the ether left 11.3 g. (85.5% of theory, taking into account 5.2 g. of original material recovered from first ether extract) of brown oil which solidified on cooling and scratching and which melted at 57.8 - 59.3° after recrystallization from aqueous alcohol containing Darco (cf. Table VII).

Anal. Calcd. for $C_{16}H_{13}NS$: S, 12.76. Found: S, 12.59.

TABLE VII

Reduction of Phenyl 1-Nitro-2-naphthyl sulfide

				Yield of amino-sulfide		
Run No.	Wt. of Nitro-sulfide (g.)	Wt. of $SnCl_2 \cdot 2H_2O$ (g.)	Wt. of Recovered Nitro-sulfide (g.)	(g.)	%	% Based on Reacted Nitro-sulfide
1	10.0	27.0	2.5	5.3	59.5	79.0
2	20.0	54.0	5.2	10.7	60.0	81.0
3	20.0	54.0	5.2	11.9	66.5	90.0
4	44.0	120.0	7.9	30.0	76.5	93.0
5	44.0	120.0	-	29.3	74.5	-
6	31.5	86.0	-	22.0	78.5	-

p-Tolyl 1-amino-2-naphthyl sulfide (IV).-This compound, prepared in an analogous manner in 76.3% yield, melted at 54.1 - 55.1° after recrystallization from aqueous alcohol containing Darco (cf. Table VIII).

Anal. Calcd. for $C_{17}H_{15}NS$: N, 5.27. Found: N, 5.29, 5.15.

The reduction of (II) was tried by several other methods, all of which were unsuccessful. Refluxing an alcoholic solution of (II) with calcium chloride and zinc dust gave a product which could not be purified. An attempted reduction of the nitro-compound with sodium sulfide and sulfur in aqueous solution was also unsuccessful since only the starting material could be obtained at the completion of the process.

Table VIII

Reduction of p-Tolyl 1-Nitro-2-naphthyl Sulfide

Run No.	Wt. of Nitro-sulfide (g.)	Wt. of $SnCl_2 \cdot 2H_2O$ (g.)	Wt. of Recovered Nitro-sulfide (g.)	Yield of amino-sulfide (g.)	%	% Based on Reacted Nitro-sulfide
1	4.2	9.0	0.9	2.4	63.0	80.0
2	7.0	18.2	1.5	4.1	66.5	82.0
3	7.0	19.3	1.7	4.3	68.5	89.5
4	7.0	20.9	0.8	4.6	73.0	82.0
5	7.0	18.2	1.3	4.3	68.5	84.5
6	11.2	29.2	2.1	7.4	73.5	90.0
7	62.0	161.2	9.2	41.0	73.5	85.5
8	11.7	30.6	2.4	7.3	69.5	87.0

Attempted ring-closure by diazotization of (III).-A suspension of 12.9 g. of (III) in 390 ml. of a 50% (by vol.) solution of sulfuric acid was boiled several minutes and then cooled rapidly. It was diazotized at -10 to 0° with a solution of 5.1 g. of sodium nitrite in 51 ml. of water, stirred for an additional two hours and then refluxed for seven hours with a solution of 132 ml. of concd. sulfuric acid in 330 ml. of water (ultimate concentration 50%). The resulting oil was extracted with ether and the ether solution, after washing with water, was dried over a large excess of anhydrous magnesium sulfate. The ether was distilled in the presence of the magnesium sulfate and the resulting black residue was extracted with ligroin in a Soxhlet extractor. This solution was chromatographed over Brockmann alumina and the chromatogram was developed with a 50% (by vol.) solution of ligroin in benzene after which the separate bands were extracted with ether. After development, the following four bands were obtained: (1) a black band, (2) a brick red band, (3) an orange band and (4) a pale yellow band. The material from the upper two bands was not investigated further. The lowest band yielded 232.5 mg. of a yellow compound insoluble in Claisen's alkali which melted at 173.7 - 175.2° after recrystallization from glacial acetic acid (cf. Table IX).

Anal. Calcd. for $C_{16}H_{10}S$: S, 13.68. Found: S, 11.59, 11.51*, 11.39*.

The compound from band 4 (above) was oxidized with excess hydrogen peroxide in glacial acetic acid solution on a boiling water bath for six hours and the resulting yellow compound melted at 258.4 - 259.7°.

Anal. Calcd. for $C_{16}H_{10}O_2S$: S, 12.04. Found: S, 10.85.

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*Analysis by Dr. Carl Tiedcke.

Table IX

Attempted Ring-closure of Phenyl 1-amino-2-naphthyl sulfide

Run No.	Wt. of Amino sulfide (g.)	Wt. of Reaction Product (g.)	Wt. of Phenyl 1-hydroxy-2-naphthyl sulfide (mg.)	Wt. of Product from Band 4 (mg.)
1	4.3	-	-	3.0
2	5.0	5.1	Total of 379.4 mg. from Runs 2 - 4	0
3	12.9	-		232.5
4	18.6	-		0

<u>Phenyl 1-hydroxy-2-naphthyl sulfide (VII).</u>-The material from the ether extraction of the third chromatographic adsorption band was soluble in Claisen's alkali and was obtained in 1% yield from (III). After recrystallization from glacial acetic acid, (VII) was obtained as yellow crystals melting at 161.5 - 163.0°.

Anal. Calcd. for $C_{16}H_{12}OS$: S, 12.71. Found: S, 12.22, 12.19.

<u>Attempted ring-closure by diazotization of (IV).</u>-Approximately 1 mg. of a pale yellow compound melting at 221.4 - 225.4° was obtained in an analogous manner from 2.5 g. of (IV). This compound, insoluble in Claisen's alkali, was not available in sufficient quantity for further investigation.

<u>p-Tolyl 1-hydroxy-2-naphthyl sulfide (VIII).</u>-This compound was obtained in a manner similar to that used for the isolation of (VII) and, after recrystallization from aqueous acetic acid, the brilliant yellow crystals melted at 131.3 - 132.1°. Yield, 6.5%.

Anal. Calcd. for $C_{17}H_{14}OS$: S, 12.04. Found: S, 11.96.

Phenyl 1-chloro-2-naphthyl sulfide.-A solution of 10.7 g. (0.0426 mol.) of (III) in 130 ml. of glacial acetic acid was added to a solution of 3.3 g. of sodium nitrite in 24 ml. of concd. sulfuric acid at a temperature of 5° - 15° after which the mixture was stirred for an additional two hours. The diazonium mixture was then added to a solution of 8.5 g. of cuprous chloride (6) in 85 ml. of concd. hydrochloric acid over a period of ten to fifteen minutes. After standing over night the solid material was filtered off and extracted with ether after which the ether solution was washed with water and dried over magnesium sulfate. The amine present (2 g.) was precipitated as its hydrochloride by treatment with dry hydrogen chloride. After washing and drying the residual ether solution, it was concentrated to a small volume and 0.8 g. of crystals filtered off and recrystallized twice from aqueous acetic acid. The salmon colored compound melted at 182.2 - 183.9°.

Anal. Calcd. for $C_{16}H_{11}ClS$: S, 11.84. Found: S, 11.79.

Phenyl 1-bromo-2-naphthyl sulfide (1.4 g., 8.7%) was obtained in an analogous manner as a salmon colored compound melting at 208.8 - 210.7° after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{16}H_{11}BrS$: S, 10.17. Found: S, 9.95.

6.3 g. of an amino hydrochloride were obtained in this reaction and after converting to the free amine, it melted at 213.9 - 216.8°. The analysis of this compound corresponds to the formula for phenyl 1-amino-2-naphthyl sulfoxide.

Anal. Calcd. for $C_{16}H_{13}ONS$: S, 11.99. Found: S, 12.28.

o-Bromo-p-thiocresol.-This compound was prepared in 67% yield from the hydrochloride of o-bromo-p-toluidine (12) by conversion to the thioxanthate ester (13, 15) and subsequent alkaline saponification in a nitrogen atmosphere. The mercaptan was identified by oxidizing it to the disulfide in alcoholic ammonia solution. After recrystallization from alcohol, the colorless disulfide melted at 99.5 - 101.0°.

Anal. Calcd. for $C_{14}H_{12}Br_2S_2$: S, 15.86. Found: S, 15.42.

Zincke and Frohneberg (20) report that this compound melts at 88° and that its isomer (the disulfide of 3-bromo-4-methyl thiophenol) melts at 100°. Since there should be no doubt about the structure of the compound prepared by the method described above, it is believed that these authors' compounds (VIII) and (XXI) should be interchanged.

o-Bromo-p-tolyl 1-nitro-2-naphthyl sulfide (IX).-This compound, prepared in 77% yield by the same method as that used for (I), melted at 122.1 - 123.0° after recrystallization from alcohol.

Anal. Calcd. for $C_{17}H_{12}O_2NBrS$: S, 8.57. Found: S, 8.74.

o-Bromo-p-tolyl 1-amino-2-naphthyl sulfide (X).-Using the same method as that for (III), this compound was prepared in 78% yield and melted at 83.5 - 84.5° after recrystallizing twice from alcohol.

o-Bromo-p-tolyl 1-acetamino-2-naphthyl sulfide was prepared by acetylation of the corresponding amine with acetic anhydride in glacial acetic acid solution and melted at 199.2 - 200.4° after recrystallization from alcohol.

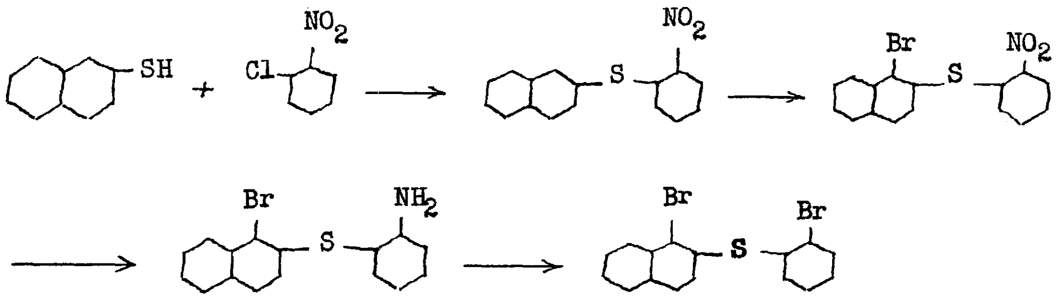
Anal. Calcd. for $C_{19}H_{16}ONBrS$: S, 8.30. Found: S, 8.32.

CONCLUSIONS

The methods outlined and attempted for the synthesis of 3,4-bonzo-9-thiafluorene are desirable because they eliminate the possibility of the formation of isomers and also because the starting materials can be made easily and in good yields.

One of the steps in the three methods requires the diazotization of an 1-amino-2-naphthyl sulfide. From the results of the Sandmeyer reactions on phenyl 1-amino-2-naphthyl sulfide it can be postulated that the poor yields in the ring-closure reaction are due to the failure of the diazotization reaction to take place to a considerable extent. It would seem, from the amount of phenyl 1-amino-2-naphthyl sulfoxide obtained in the Sandmeyer reaction, that a large amount of the nitrous acid is used in the oxidation of the amino-sulfide to the corresponding sulfoxide. In view of these results, it might be possible to diazotize the amino-sulfoxide and carry out the ring-closure reaction after which the sulfoxide could be either reduced to the sulfide or oxidized to the sulfone.

A series of reactions, which might lead to the compound necessary for ring-closure by the third method described previously, can be outlined as follows:



Bromination of the nitro-sulfide should not be complicated by addition of bromine to the sulfur, as is usually the case with unsubstituted sulfides, since it was found that phenyl 1-nitro-2-naphthyl sulfide did not add bromine. It is also anticipated that diazotization of the amino-group on the phenyl nucleus could be carried out in better yield than the compound containing an amino-group on the no. 1 - C of the naphthalene nucleus. Various other possibilities present themselves but this one seems to be the most promising.

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