[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Oxidation of Dibenzothiophene and Phenoxathiin with Hydrogen Peroxide

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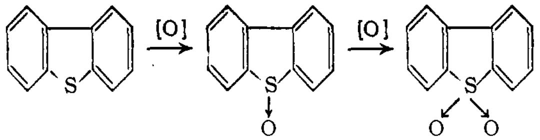
The use of hydrogen peroxide (30% aqueous solution) for the oxidation of dibenzothiophene to dibenzothiophene-5-oxide and -5-dioxide and of phenoxathiin to phenoxathiin-10-oxide and -10-dioxide in glacial acetic acid or ethanol solution has been investigated. Reaction conditions which give optimum yields of the sulfoxides and sulfones were determined. The results of comparative studies showed phenoxathiin to be more easily oxidized than dibenzothiophene.

The oxidation of sulfides with hydrogen peroxide (30% aqueous solution) is a very satisfactory method for the preparation of many sulfoxides and sulfones.[1,2] A review of the literature, however, reveals numerous instances where this procedure was only partially successful, or even failed entirely. For example, under identical conditions,[3] diphenyl sulfide and diphenylmethyl phenyl sulfide were readily oxidized to the corresponding sulfones, while dibenzyl sulfide, diamyl sulfide and diphenylmethyl α-naphthyl sulfide yielded only the sulfoxides and triphenylmethyl phenyl sulfide and di-α-naphthyl sulfide showed no reaction. In the case of heterocyclic sulfides, a recent report[4] shows that although 5-nitrothianaphthene was readily oxidized to the 1-dioxide, 3-nitro-, 3,5-dinitro- and 3,5,7-trinitrothianaphthene were recovered unchanged. In addition, it was reported[5a] that 2,8-diacetaminodibenzothiophene could not be oxidized with hydrogen peroxide until an excess of acetic anhydride had been added, and the tetraacetyl derivative apparently had been formed, although later workers[5b] were able to carry out the oxidation successfully using either hydrogen peroxide or sodium hypochlorite in glacial acetic acid solution.

In connection with a general study of sulfides, sulfoxides and sulfones, it seemed of interest to compare the ease of oxidation with hydrogen peroxide of dibenzothiophene and phenoxathiin, and at the same time to determine the optimum conditions for the preparation of the corresponding sulfoxides and sulfones. Some of our results are now being presented in view of the recent report[6] that dibenzothiophene-5-dioxide was not obtained by refluxing a mixture of dibenzothiophene, glacial acetic acid and excess hydrogen peroxide (30% aqueous solution) for one hour. Our studies have confirmed the work previously reported from this Laboratory[7] which showed that quantitative yields of the dioxide were obtained under essentially the same conditions. Two possible explanations of the discrepancy in results obtained are: (1) that the solution of oxidizing agent used in the unsuccessful runs did not contain 30% of hydrogen peroxide[8] but was of sufficient strength to oxidize dibenzothiophene only to the monoxide, or (2) that a stabilizing agent was present in the peroxide solution which may have permitted oxidation to the monoxide but inhibited formation of the dioxide.

In Tables I and II are given the data on the oxidation of dibenzothiophene under varied conditions. The results indicate that the extent of oxidation of dibenzothiophene depends upon the oxidizing agent added, the solvent used, the reaction time and temperature employed, and whether or not the reaction mixture is stirred, either mechanically or by vigorous refluxing. We were able to duplicate the preparation of dibenzothiophene-5-oxide by the procedure of Schlesinger and Mowry[6] provided that vigorous refluxing was employed, and provided that the refluxing was discontinued immediately after the mixture of dibenzothiophene, hydrogen peroxide and glacial acetic acid became homogeneous. If the refluxing was not vigorous, a white precipitate appeared in the solution before all of the molten dibenzothiophene was dissolved, and dibenzothiophene, dibenzothiophene-5-oxide and dibenzothiophene-5-dioxide were isolated. When the period of vigorous refluxing was continued for even a few minutes after homogeneity was obtained, the product isolated was a mixture of monoxide and dioxide, and a total reflux time of 30 minutes repeatedly gave excellent yields of the dioxide. The use of two different commercial brands of 30% aqueous hydrogen peroxide[9] did not materially affect the results. Optimum yields of both the monoxide and the dioxide were obtained when the mixture was stirred mechanically while refluxing.

It should be noted that our results indicate that the oxidation of the sulfide linkage in dibenzothiophene is a stepwise process. This mechanism finds some support in the work of Böeseken and Arrias[10] who found that with the related diphenyl sulfide, the rate of oxidation to the sulfoxide with acetyl peroxide is several hundred times greater than the



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(1) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons. Inc., New York, N. Y., 1943, pp. 870, 874.

(2) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 666.

(3) P. Knoll, *J. prakt. Chem.*, **113**, 40 (1926). The oxidations were carried out at room temperature with hydrogen peroxide in glacial acetic acid. The observed results appear to hold only for the specific method employed, since J. A. Smythe (*J. Chem. Soc.*, **101**, 2076 (1912)) and C. Courtot and Paivar (*Chimie & industrie*, **45**, 80 (1941)) report the use of somewhat related conditions for the preparation of dibenzyl sulfone and di-α-naphthyl sulfone, respectively.

(4) F. G. Bordwell and C. J. Albisetti, THIS JOURNAL, **70**, 1955 (1948).

(5) (a) C. R. Neumoyer and E. D. Amstutz, *ibid.*, **69**, 1920 (1947); (b) H. Gilman and J. F. Nobis, *ibid.*, **71**, 274 (1949).

(6) A. H. Schlesinger and D. T. Mowry, *ibid.*, **73**, 2614 (1951).

(7) H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945).

(8) From experience we have found it advisable to analyze (by permanganate titration) the peroxide solutions used in order to guard against possible deterioration. Although the peroxide content is usually found to be at least 30%, on one occasion titration of a commercial sample immediately after opening the sealed cap showed the presence of only 4.5% of hydrogen peroxide.

(9) J. T. Baker Analyzed, C.P. and Merck "Superoxol."

(10) J. Böeseken and E. Arrias, *Rec. trav. chim.*, **54**, 711 (1935).

TABLE I

OXIDATION OF DIBENZOTHIOPHENE WITH HYDROGEN PEROXIDE IN GLACIAL ACETIC ACID

No.	Dbt,[a] g., mole	AcOH, ml.	H_2O_2,[b] ml.	T, °C.	Reaction time,[c] min.	Recovery or yield,[d] % Dbt	Dbt-5-oxide	Dbt-5-dioxide
1	10.0, 0.054	75	6.2[e]	90 and 98	20[f]	67.0	12.0	..
2	18.4, 0.1	100	40	Reflux	90[g,h]	..	...	97.2
3	27.6, 0.15	150	60	Reflux[i]	90[h,j]	..	...	92.8
4	20.0, 0.109	75	62[k]	Reflux	10[l]	21.5	11.0	55.8
5	20.0, 0.109	75	62[m]	Reflux	6[n]	8.0	62.4[o]	..
6	20.0, 0.109	75	62[k]	Reflux[i]	5[p]	13.0	71.5[q]	..
7	20.0, 0.109	75	62[k]	Reflux	10[r]	..	41.8[s]	31.5
8	20.0, 0.109	75	62[k]	Reflux	30[t]	..	...	92.4[u]

[a] Dbt, dibenzothiophene (Eastman Kodak Company, White Label). [b] 30% aqueous solution. [c] Total time after addition of the hydrogen peroxide was complete unless otherwise indicated. [d] The products were obtained by filtering the cooled reaction mixture or by diluting with water, then cooling and filtering. Dbt was obtained from mixtures by extraction with cold petroleum ether (b.p. 28–38°). Dilute ethanol was found to be the best recrystallization solvent for dbt, benzene for dbt-5-oxide, and glacial acetic acid for dbt-5-dioxide. Identity of all products was established by the method of mixed melting points. [e] A 10% excess over 1.0 equivalent. [f] The hydrogen peroxide was added at 80°. The temperature was then maintained at 90° for 10 min. and finally at 98° for 10 min. [g] Thirty ml. of hydrogen peroxide was added to the hot solution. After refluxing for 1 hr., an additional 10 ml. was added. The mixture was allowed to stand overnight at room temperature. [h] A copious precipitate appeared after refluxing about 30 min. [i] With stirring. [j] Forty-five ml. of hydrogen peroxide was added to the stirred, refluxing solution. After refluxing for 1 hr., an additional 15 ml. of peroxide was added. [k] 0.60 mole of J. T. Baker Analyzed, C.P. [l] The reagents were mixed at room temperature, then warmed to 106° (reflux temperature) and maintained at only a gentle reflux for 10 min. Molten dbt remained undissolved in the bottom of the reaction flask, and considerable precipitate had appeared in the upper portion of the mixture. After cooling in a cold water-bath until refluxing ceased, the mixture was poured into 200 ml. of water, cooled to room temperature and filtered. [m] 0.60 mole of Merck "Superoxol." [n] Same as (*l*) except that the mixture was warmed to 106° over a period of 15 min. and refluxed vigorously until the mixture became homogeneous. [o] Recrystallized once from benzene. Reduction in the volume of the benzene filtrate gave an additional 20.2% of only slightly impure monoxide. The dbt was isolated by removal of the remaining benzene and recrystallization of the residue from dilute ethanol. The crude yield of dbt-5-oxide was 95.7%. [p] Same as *n* except that the stirred mixture became homogeneous in 3 min., after which stirring and vigorous refluxing were continued for 2 min. [q] After two recrystallizations from ethanol. The dbt was isolated by dilution of the ethanol filtrates. The crude yield was 97.8%. The crude yield from a check run was 96.7%, and one recrystallization from benzene gave 78.8% of pure monoxide with an additional 15.1% of only slightly impure material being obtained on reduction in the volume of the filtrate. [r] Same as *l* except that vigorous refluxing was employed and that the mixture became homogeneous in 6 min. and remained so for the additional 4 min. of refluxing. [s] From ethanol. The mixture was readily separated due to the insolubility of the dioxide in refluxing ethanol. [t] Same as *n* except that vigorous refluxing was maintained for 30 min. The mixture became homogeneous in 6 min., and a copious precipitate appeared in 14 min. A check run using Merck "Superoxol" gave nearly identical results. In another check run in which stirring was employed, the mixture became homogeneous in 3 min., a precipitate appeared in 12 min., and the initial product was nearly pure dbt-5-dioxide. [u] After one recrystallization from glacial acetic acid.

TABLE II

MISCELLANEOUS OXIDATIONS OF DIBENZOTHIOPHENE

No.	Dbt,[a] g., mole	Solvent, ml.	Oxidizing agent	T, °C.	Reaction time,[b] hr.	Recovery or yield,[c] % Dbt	Dbt-5-oxide	Dbt-5-dioxide
1	45, 0.25	CCl_4, 400	Cl_2,[d] 18 g.	0–5	0.17	..	50.2[e]	...
2	9.2, 0.05	EtOH,[f] 250	H_2O_2,[g] 50 ml.	Reflux	6.0[h]	56.6	34.0	...
3	9.2, 0.05	EtOH,[f] 250	H_2O_2, 70 ml.	Reflux	49.0[i]	..	64.0[j]	33.3[j]
4	9.2, 0.05	EtOH,[k] 300	H_2O_2, 30 ml.	Reflux	5.0[l]	91.2	...	...
5	9.2, 0.05	Me_2CO,[m] 300	H_2O_2, 30 ml.	Reflux	4.0[n]	94.6	...	...

[a] Dbt, dibenzothiophene (Eastman Kodak Company, White Label). [b] Total reaction time after adding the oxidizing agent unless otherwise indicated. [c] See footnote *d*, Table I. [d] R. K. Brown, R. Christianson and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948). [e] The crude yield was 71.8%. [f] In general accordance with the directions of F. Kehrmann and L. Diserens, *Ber.*, **48**, 318 (1915), for the oxidation of substituted phenothiazines to the monoxide derivatives. [g] 30% aqueous solution. [h] Thirty ml. of hydrogen peroxide was added to the refluxing solution. After refluxing for 1.5 hours, an additional 20 ml. of peroxide was added and refluxing was continued for 4.5 hours. The solution was then allowed to stand overnight at room temperature. [i] Thirty ml. of hydrogen peroxide was added to the refluxing solution. After refluxing 3 hr., an additional 20 ml. of peroxide was added. The solution was then refluxed for 14 hr., after which another 20 ml. of peroxide was added, refluxing was continued for 32 hr., and the solution was finally allowed to stand overnight at room temperature. [j] Crude yield. [k] In general accordance with the directions given by R. Pummerer and S. Gassner, *Ber.*, **46**, 2322 (1913), for the oxidation of phenothiazine to the monoxide derivative, 4 ml. of 10% alcoholic KOH was added to this run. [l] Twenty ml. of hydrogen peroxide was added slowly at room temperature (vigorous frothing occurred during the addition). After refluxing for 4 hr., an additional 20 ml. of peroxide was added. The solution was refluxed for one hour longer and then allowed to stand overnight at room temperature. [m] In general accordance with the directions given by E. B. Barnett and S. Smiles, *J. Chem. Soc.*, **95**, 1265 (1909), for the oxidation of phenothiazine to the monoxide derivative, a few drops of an ethanolic solution of sodium ethoxide was added to the acetone solution of dbt. [n] Twenty ml. of hydrogen peroxide was added to the refluxing solution. After refluxing for 2 hr., an additional 10 ml. of peroxide was added, and the solution was refluxed for 2 hr. longer. The solvent was removed and the residue was recrystallized from dilute ethanol.

subsequent oxidation of the sulfoxide to the sulfone.

In Table III are listed the data on the oxidation of phenoxathiin under varied conditions. In general, the same considerations and conclusions apply that were discussed above for dibenzothiophene. A comparison of the results in Tables I, II and III indicates that the oxidation of phenoxathiin to either the monoxide or the dioxide proceeds more readily than does the corresponding oxidation of dibenzothiophene. This conclusion is firmly es-

TABLE III

OXIDATION OF PHENOXATHIIN WITH HYDROGEN PEROXIDE IN GLACIAL ACETIC ACID

No.	Phn,[a] g., mole	AcOH, ml.	H_2O_2,[b] ml.	T, °C.	Reaction time,[c] min.	Recovery or yield,[d] % Phn	Phn-10-oxide	Phn-10-dioxide
1	10.0, 0.05	50	15	90, Reflux	90[e]	..	...	88.6
2	10.0, 0.05	50	15	90	60[f]	12.0	81.4[g]	..
3	10.0, 0.05	50	6[h]	90, 98	40[i]	49.0	40.0	..
4	10.0, 0.05	75	15	Reflux	20[j]	..	12.4	71.8
5	10.0, 0.05	75	15	Reflux	10[k]	..	50.5	34.9
6	10.0, 0.05	75	15	Reflux	2[l]	..	84.8[g]	..
7	20.0, 0.10	75	62	Reflux	0[m]	..	58.3[n]	..
8	20.0, 0.10	75	62	Reflux	30[o]	..	...	97.0

[a] Phn, phenoxathiin (A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 485). [b] 30% Aqueous solution. [c] Total reaction time after addition of the hydrogen peroxide unless otherwise indicated. [d] The products were obtained by filtering the cooled reaction mixture or by diluting with water, then cooling and filtering. Phn was isolated from mixtures by extraction with cold petroleum ether (b.p., 60–70°). Methanol was found to be a satisfactory recrystallization solvent for phn, methanol or dilute acetic acid for phn-10-oxide, and glacial acetic acid for phn-10-dioxide. Identity of all products was established by the method of mixed melting points. [e] The hydrogen peroxide was added at 80°. The solution was heated at 90° for one hr., then refluxed for 0.5 hr., poured into 50 ml. of water, cooled, and filtered. [f] Same as *e* except that refluxing was omitted. [g] Crude yield. [h] A 10% excess over 1.0 equivalent. [i] The hydrogen peroxide was added at 80°. The solution was heated at 90° for 10 min., then at 98° for 10 min., and finally diluted slightly with water, cooled and filtered. [j] The hydrogen peroxide was added dropwise to the stirred, refluxing solution. After refluxing for 20 min., the solution was poured into 150 ml. of water, cooled, and filtered. [k] Same as *j* except that refluxing was continued for only 10 min. after addition of the peroxide was complete. [l] Same as *j* except that refluxing was continued for only 2 min. after addition of the peroxide was complete. [m] The stirred mixture of phn and glac. AcOH was warmed to 100°. The peroxide was added and the mixture was brought to a vigorous reflux (106°). Stirring and heating were immediately discontinued and the solution was poured into 250 ml. of water, cooled and filtered. [n] One recrystallization from benzene. An additional 37.9% of impure phn-10-oxide was isolated from the filtrate. A check run gave a 57.4% pure yield plus a 28.2% yield of impure material. In another run which differed only in that the reagents were mixed at room temperature, the pure yield of monoxide was 47.7% plus a 35.2% yield of impure product. [o] The reagents were mixed at room temperature, then stirred and warmed to 106°. After refluxing for 30 min., the solution was allowed to stand overnight at room temperature. Filtration gave 86.2% of pure phn-10-dioxide with an additional 10.8% being recovered by dilution of the filtrate. In another run in which the solution was poured into 250 ml. of water after the 30 min. period of reflux, a 98.6% crude yield was obtained. Recrystallization from glac. AcOH gave an 83.1% pure yield and 10.8% of slightly impure material was isolated by dilution of the filtrate.

TABLE IV

COMPARATIVE OXIDATION OF DIBENZOTHIOPHENE AND PHENOXATHIIN BY HYDROGEN PEROXIDE

No.	Sulfide[a]	Solvent,[b] ml.	H_2O_2,[b,c] ml.	T, °C.	Reaction time	Recovery or yield,[d] % Sulfide	Monoxide	Dioxide
1	dbt	AcOH, 50	15	90	60 min.[e]	1.3	92.0[f]	..
	phn					..	89.9[f]	1.6
2	dbt	AcOH, 75	25	90; Reflux	75 min.[g]	..	...	78.3
	phn					..	...	90.1
3	dbt	AcOH, 75	25	90; Reflux	75 min.[h]	..	...	97.3
	phn					..	...	97.9
4	dbt	AcOH, 75	15	Reflux	7 min.[i]	20.7	57.3	..
	phn					..	77.9	..
5	dbt	EtOH, 250	50	Reflux	12 hr.[j]	89.2	...	..
	phn					..	98.1	..
6	dbt	EtOH, 250	50	Reflux	19 hr.[k]	86.8	..	..
	phn					..	95.5	..

[a] The runs were all made with 0.05 mole of each sulfide. Dbt, dibenzothiophene (Eastman Kodak Company, White Label); phn, phenoxathiin (see footnote *a*, Table III). [b] The indicated amount was used for each sulfide. [c] 30% Aqueous solution. [d] See footnote *d*, Table I; footnote *c*, Table II; and footnote *d*, Table III for the procedures used in isolating, purifying and identifying the products obtained. [e] The hydrogen peroxide was added at 80°. The temperature was then maintained at 90° for one hour, after which the reaction mixtures were poured into flasks packed in ice and filtered after thorough cooling. [f] Crude yield. [g] Fifteen ml. of hydrogen peroxide was added to each solution at 80°. The solutions were heated at 90° for 30 min., then refluxed for 30 min. An additional 10 ml. of hydrogen peroxide was added to each, and refluxing was continued for 15 min. The solutions were poured into 150 ml. of water each, cooled and filtered. [h] Same as *g* except that the solutions were stirred throughout. [i] The hydrogen peroxide was added dropwise to the stirred refluxing solutions over a period of 5 min. Refluxing was continued for two minutes, after which the solutions were poured into 150 ml. of water each, cooled and filtered. [j] Thirty ml. of hydrogen peroxide was added to each refluxing solution. After refluxing 3 hours, an additional 20 ml. of hydrogen peroxide was added to each solution, refluxing was continued for 9 hours more, and the solutions were allowed to stand overnight at room temperature. [k] Same as *j* except that the solutions were refluxed 16 hours after the second addition of hydrogen peroxide.

tablished by an inspection of the data given in Table IV. The results of Runs 5 and 6, Table IV, are particularly noteworthy since they show that, under the same conditions of time and temperature, hydrogen peroxide in ethanol solution does not oxidize dibenzothiophene appreciably, yet oxidizes phenoxathiin almost completely to the monoxide.

Experimental

The following are descriptions of typical preparations in which the procedure used was such as to give optimum yields of the desired dibenzothiophene-5-oxide or -dioxide or phenoxathiin-10-oxide or -dioxide.[11] The identity of all

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[11] The results of each run were checked by Travis Stevens and Gene R. Wilder.

products was established by the method of mixed melting points. All melting points are uncorrected.

Dibenzothiophene-5-oxide.—A stirred mixture of 20.0 g. (0.109 mole) of dibenzothiophene, 75 ml. of glacial acetic acid and 62 ml. of hydrogen peroxide (30% aqueous solution) was brought to a vigorous reflux (106°) and maintained at this temperature until the mixture became homogeneous (4 min.). Stirring and heating were immediately discontinued. After cooling slightly, the solution was poured into 200 ml. of water, and the resulting mixture was cooled under the tap and filtered. The crude product weighed 20.9 g. (95.7%) and melted at 174–180°. One recrystallization from benzene gave 17.2 g. (78.8%) of dibenzothiophene-5-oxide, m.p. 186–187°. Additional less pure material was isolated from the benzene filtrate.

Dibenzothiophene-5-dioxide.[7]—A stirred mixture of 20.0 g. (0.109 mole) of dibenzothiophene, 75 ml. of glacial acetic acid and 62 ml. of hydrogen peroxide (30% aqueous solution) was refluxed vigorously (106°) for 30 min. (homogeneity in 4 min.; copious precipitate at the end of 12 min.), then allowed to stand overnight at room temperature. Filtration gave 22.6 g. (97.2%) of pure dibenzothiophene-5-dioxide, m.p. 232–233°.[12]

Phenoxathiin-10-oxide.[13]—To a refluxing solution of 10.0 g. (0.05 mole) of phenoxathiin in 250 ml. of absolute ethanol was added 30 ml. of hydrogen peroxide (30% aqueous solution). After refluxing on the steam-bath for three hours, an additional 20 ml. of peroxide was added. Refluxing was continued for 9 hours more, and the solution was then allowed to stand at room temperature overnight. The solution was reduced in volume to 75 ml. and diluted hot just to turbidity with hot water. Cooling and filtration yielded 10.6 g. (98.1%) of pure phenoxathiin-10-oxide, m.p. 152–153°.

Phenoxathiin-10-dioxide.[14]—A stirred mixture of 20.0 g. (0.10 mole) of phenoxathiin, 75 ml. of glacial acetic acid and 62 ml. (0.60 mole) of hydrogen peroxide (30% aqueous solution) was refluxed (106°) for one hour, then allowed to stand at room temperature overnight.[15] Filtration gave 20.0 g. (86.2%) of phenoxathiin-10-dioxide melting at 147–148°. Dilution of the filtrate with water yielded an additional 2.5 g. (10.8%) of product, m.p. 146–147°.

The comparative ease with which phenoxathiin is oxidized to either the monoxide or the dioxide lends support to the possibility that the reported[16] preparation of 4-aminophenoxathiin hydrochloride by the Hofmann reaction may have yielded the monoxide derivative instead. A recalculation of the theoretical percentages of nitrogen shows that the per cent. of nitrogen found by analysis corresponds much more closely to that calculated for 4-aminophenoxathiin-10-oxide hydrochloride than to that calculated for either the unoxidized compound or for the dioxide.[17] Since the sodium hypochlorite that is present while the Hofmann reaction is being run has been shown[5a,18] to oxidize various sulfides to sulfoxides or sulfones, 4-aminophenoxathiin-10-oxide hydrochloride may have been the compound obtained. However, since the same compound was obtained by the reaction of 4-phenoxathiinyllithium with α-methylhydroxylamine (conditions not usually considered as oxidizing), formation of the unoxidized compound is indicated. This contention is supported by the fact that the preparation of 4-aminodibenzothiophene *via* the Hofmann reaction has resulted in a 48% yield of the unoxidized compound, the identity being established by the lack of depression in the melting point when a portion of the product was mixed with a sample of authentic material.[19] Under the oxidizing conditions of the Hofmann reaction, the isolation of 4-aminophenoxathiin-10-oxide hydrochloride would not be inconsistent with the isolation of 4-aminodibenzothiophene, however, since phenoxathiin has been shown to undergo oxidation more readily than dibenzothiophene.

4-Dibenzothiophenecarboxylic Acid Amide.—Sixteen grams (0.07 mole) of 4-dibenzothiophenecarboxylic acid[19a] was converted to the 4-dibenzothiophenecarboxylic acid chloride[20] by dissolving in 26 ml. of freshly distilled thionyl chloride and refluxing for one hour. After removal of the excess thionyl chloride by distillation, the crude acid chloride was allowed to stand overnight with 200 ml. of concentrated ammonium hydroxide. Filtration yielded 15.5 g. (98.4%) of crude amide melting at 240–242°. Two recrystallizations from dioxane gave 8.0 g. (50.8%) of pure 4-dibenzothiophenecarboxylic acid amide, m.p. 250–251°.

Anal. Calcd. for $C_{13}H_9ONS$: S, 14.07. Found: S, 13.81.

4-Dibenzothiophenecarboxamide-5-dioxide.—A stirred mixture of 7.0 g. (0.03 mole) of 4-dibenzothiophenecarboxylic acid amide and 200 ml. of glacial acetic acid was warmed to 80° and 10 ml. of hydrogen peroxide (30% aqueous solution) was added. After refluxing for one hour, an additional 10 ml. of peroxide was added and refluxing was continued for 30 minutes more. The volume of the solution was reduced to 100 ml. by distillation and cooled rapidly with vigorous stirring. Filtration gave 6.2 g. (77.5%) of 4-dibenzothiophenecarboxamide-5-dioxide melting at 236–238°. The melting point remained unchanged on recrystallizing the product from methanol.

Anal. Calcd. for $C_{13}H_9O_3NS$: S, 12.37. Found: S, 12.21.

4-Aminodibenzothiophene.—This compound has been prepared previously[19] by the Bucherer reaction, by amination of 4-bromodibenzothiophene, and by the reaction of 4-dibenzothienyllithium with α-methylhydroxylamine. The present preparation was made in essential accordance with the procedure used for the preparation of 4-aminophenoxathiin by the Hofmann reaction.[16] A solution of 4.3 g. (0.027 mole) of bromine and 5.3 g. (0.132 mole) of sodium hydroxide in 45 ml. of water was added to a suspension of 5 g. (0.022 mole) of 4-dibenzothiophenecarboxylic acid amide in 45 ml. of dioxane and 30 ml. of 10% sodium carbonate. The solution was heated on the water-bath for 12 hours, then cooled and extracted with ether. The crude amine hydrochloride was precipitated by passing hydrogen chloride into the dried ether extract. Filtration gave 3.5 g. (67.4%) of crude 4-aminodibenzothiophene hydrochloride melting at 243–248°. This product was suspended in 500 ml. of dilute (1:10) ammonium hydroxide and allowed to stand overnight. The yield of crude 4-aminodibenzothiophene melting at 103–106° was 4.4 g. (63.9%). One recrystallization from dilute methanol gave 2.1 g. (48.0%) of pure amine, m.p. 109–110°. A mixed melting point with an authentic specimen[19] was not depressed.

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[12] In another experiment in which the mixture was poured into 200 ml. of water after the 30 min. period of reflux, a 99.2% yield of crude product melting at 228–230° was obtained. Recrystallization from glacial acetic acid gave a 91.7% yield of pure dioxide.[11]

[13] See also Run 7, Table III.[11]

[14] See H. D. K. Drew, *J. Chem. Soc.*, 511 (1928), for a less complete description of a similar preparation of phenoxathiin-10-dioxide.

[15] In another run, the solution was refluxed 30 min., then poured into 250 ml. of water. Although the initial product was slightly impure, recrystallization from glacial acetic acid gave an 83.1% yield of pure phenoxathiin-10-dioxide.[11]

[16] H. Gilman, M. W. Van Ess, H. B. Willis and C. G. Stuckwisch, THIS JOURNAL, **62**, 2607 (1940).

[17] *Anal.* Calcd. for $C_{12}H_{10}ONClS$: N, 5.57. Calcd. for $C_{12}H_{10}O_2NClS$: N, 5.23. Calcd. for $C_{12}H_{10}O_3NClS$: N, 4.94. Found: N, 5.17.[16]

[18] A. E. Wood and E. G. Travis, THIS JOURNAL, **50**, 1226 (1928). See, particularly, J. Weijlard, *ibid.*, **67**, 1031 (1945).

[19] (a) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) H. Gilman and S. Avakian, THIS JOURNAL, **68**, 1514 (1946).

[20] H. Gilman and S. Avakian, *ibid.*, **68**, 2104 (1946).