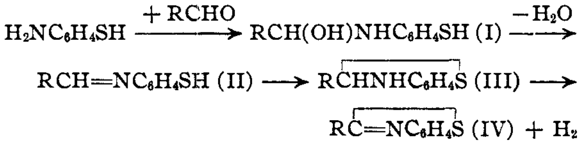
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Researches on Thiazoles. XX. The Synthesis of Benzothiazoles from Aldehydes and Ortho-aminothiophenol. The Action of Aldehydes upon Zinc Ortho-aminothiophenolate and upon Related Thionated Aromatic Amines

BY MARSTON TAYLOR BOGERT AND BARNET NAIMAN[1]

The formation of benzothiazoles by the action of aldehydes upon *o*-aminothiophenols was reported first by Hofmann,[2] and the method has been utilized frequently since.[3]

The mechanism of the reaction is probably best represented as



$$H_2NC_6H_4SH \xrightarrow{+RCHO} RCH(OH)NHC_6H_4SH \text{ (I)} \xrightarrow{-H_2O} RCH{=}NC_6H_4SH \text{ (II)} \longrightarrow RCHNHC_6H_4S \text{ (III)} \longrightarrow RC{=}NC_6H_4S \text{ (IV)} + H_2$$

In the experimental part of this paper it is shown that the anils (II) can be converted easily into the thiazoles (IV), and the recent articles by Lankelma and Sharnoff[4] make it clear that the thiazolines are intermediate products in the formation of the thiazoles from the aminothiophenols and aldehydes. The latter investigators also reported that the benzothiazolines could be oxidized easily to the corresponding benzothiazoles by ferric chloride in alcoholic solution, and that the 2-aryl benzothiazolines underwent this oxidation even during crystallization from alcohol, acetone or carbon tetrachloride.

This oxidation of the thiazolines to thiazoles interested us greatly because of certain observations made in the course of our own work and recorded beyond. Ordinarily such oxidations would be expected to take place either (1) by evolution of hydrogen as such, (2) by oxidation by the air, (3) by oxidation at the expense of some other constituent of the solution, or even (4) by oxidation of some molecules of the compound due to the simultaneous reduction of others.

In our studies of the interaction of benzaldehyde and *o*-aminothiophenol described beyond, we failed to detect the elimination of any hydrogen or to isolate any of the usual reduction products of benzaldehyde, such as benzyl alcohol, hydrobenzoins, stilbene, etc., even though careful search was made for them. The only pure products secured by us were the benzothiazoles, although in the light of the work of Lankelma and Sharnoff[4] it seems probable that the benzothiazolines must have been their immediate progenitors, the thiazolines oxidizing quickly to the thiazoles during either the preparation or the purification of the crude products.

The benzothiazoles are exceedingly difficult to reduce and of course the thiazolines would be still less likely to suffer any further hydrogenation under the conditions prevailing in these reactions. In such a simple case, therefore, as the transition of a benzothiazoline to a benzothiazole merely by crystallization from alcohol, there would appear to be but two possibilities, namely, evolution of hydrogen as such, or atmospheric oxidation. This we hope to determine as soon as a sufficient supply of the requisite thiazoline is available.

Marler[5] made the interesting observation in studying the production of 2-phenylbenzothiazole by heating thiobenzanilide to 220°, that the by-products were aniline, stilbene and hydrogen sulfide, but no hydrogen.

That, under the conditions of our experiments, the anil (II) is an intermediate product in this thiazole synthesis seems likely from the results recorded beyond.

In the preparation of 2-phenylbenzothiazole from zinc *o*-aminothiophenolate and benzaldehyde, it was observed that a suspension of this zinc salt in boiling glacial acetic acid dissolved immediately to a clear yellow solution as soon as benzaldehyde was added. It seemed scarcely probable that this change in solubility was a purely physical phenomenon, to be ascribed to the solvent action of the benzaldehyde alone, but rather that some chemical combination or reaction was responsible; and when the colorless

---

[1] Presented in abstract before the Division of Organic Chemistry at the St. Petersburg Meeting of the American Chemical Society, March 27, 1934. Based upon the Dissertation submitted by the junior author, June, 1934, for the degree of Ph.D., under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

[2] Hofmann, *Ber.*, **13**, 1236 (1880).

[3] Green and Perkin, *J. Chem. Soc.*, **83**, 1204 (1903); Bogert and Stull, THIS JOURNAL, **47**, 3078 (1925); Bogert and Corbitt, *ibid.*, **48**, 783 (1926); Bogert and Hess, *ibid.*, **48**, 904 (1926); Bogert and Allen, *ibid.*, **49**, 1315 (1927).

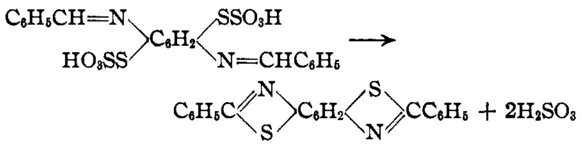
[4] (a) Lankelma and Sharnoff, THIS JOURNAL, **53**, 2654 (1931); (b) *ibid.*, **54**, 379 (1932).

[5] Marler, "Inaugural Dissertation," Hamburg, 1927, p. 33.

zinc aminothiophenolate was refluxed directly with benzaldehyde, a deep red solution was obtained, from which the benzal derivative of the zinc salt, $(C_6H_5CH{=}NC_6H_4S)_2Zn$, was separated in reddish-orange plates. Similar crystalline products were secured with other aldehydes, those with salicyl aldehyde and piperonal being bright yellow, and with fural red.

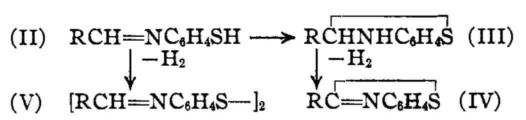
The clear yellow solution which results when the zinc aminothiophenolate and benzaldehyde interact in glacial acetic acid, is presumably due to the formation of the colorless aldol (I), which then gradually loses water, giving the darker colored anil.

Green and Perkin[6] observed that when *p*-phenylenediamine-2,5-di-(thiosulfuric acid) was heated with benzaldehyde, it formed a benzal derivative which at higher temperature yielded the benzobisthiazole as follows



Bogert and Updike[7] and Bogert and Taylor[8] have shown also that anils are intermediate products in the synthesis of benzothiazoles from aniline *o*-thiosulfuric acids and aromatic aldehydes.

In the case of the anils of the zinc *o*-aminothiophenolate studied by us, as soon as the zinc was removed, the free anil thiophenols (II) must have instantly rearranged to the benzothiazolines (III), instead of oxidizing to the disulfides (V), and the thiazolines then oxidized to the benzothiazoles (IV).



These anil zinc salts could be easily converted into the corresponding 2-R benzothiazoles by direct heating, by refluxing for ten minutes their glacial acetic acid solutions, or occasionally by boiling their solutions in 95% alcohol or even in petroleum ether.

The behavior of certain aromatic aldehydes with *o*-aminophenyl disulfide was likewise investigated and it was learned that in alcoholic solution the disulfide condenses with the aldehyde to an anil, but that when the two are heated together without any solvent, or in a solvent boiling at 140° or above, the 2-R benzothiazole is the product. Further, when a mixture of approximately equal weights of the anil and its parent aldehyde is refluxed in xylene solution, the benzothiazole again is the result.

Contrary to the behavior of the anil zinc salts of *o*-aminothiophenol, these anils of the disulfide when boiled with glacial acetic acid revert to the initial disulfide (m. p. 93°) and aldehyde and do not give the benzothiazoles.

Experimental Part

I. The Formation of Benzothiazoles from *o*-Aminothiophenols and Aldehydes

(1) By saturating a hot glacial acetic acid solution of the zinc salt with hydrogen sulfide and filtering from the zinc sulfide, an acetic acid solution was prepared containing 0.8 g. of the free *o*-aminothiophenol and sufficient hydrogen sulfide to protect it from oxidation to the disulfide. This operation was carried out in a small flask provided with a thermometer, a manometer and a dropping funnel, all of the connections being tightly sealed to prevent any leaks. Since the interaction of benzaldehyde and *o*-aminothiophenol proceeds very slowly at ordinary temperature, the acetic acid solution was kept at a temperature of approximately 26° throughout the reaction. The calculated quantity of benzaldehyde was dripped in and the reaction allowed to continue for about fifteen minutes. The pressure change registered by the manometer when the benzaldehyde was added was only 3 mm. and this did not change during the progress of the reaction. That this pressure change was due merely to the volume of the benzaldehyde added was shown by addition of the same volume of water, when the increase in pressure registered was again 3 mm., whereas if all the hydrogen represented as liberated in the reaction were set free in the gaseous condition, it would amount to about 150 cc., which would have caused an increase in pressure of about 700%.

(2) In another set of experiments, the reactions were all carried out in an atmosphere of hydrogen or hydrogen sulfide as follows. The reaction flask (A) was provided with an inlet tube for hydrogen sulfide, a stopcock funnel tube (F) and an exit tube to an empty flask (B), which latter was connected with a suction pump and, by means of a siphon, with another flask (C) containing freshly distilled water.

A solution of 3.1 g. of *o*-nitrophenyl disulfide in 350 cc. of glacial acetic acid was prepared in flask A, and to it was added slowly 20 g. of zinc dust. The hydrogen evolved was passed through the whole apparatus, to displace as much of the air as possible. When the reduction of the disulfide was complete, a rapid stream of hydrogen sulfide was passed through the whole system, including the stopcock funnel tube, to precipitate the zinc and remove the rest of the air. This current of hydrogen sulfide was kept flowing through during the entire reaction.

---

[6] Green and Perkin, *J. Chem. Soc.*, **83**, 1207 (1903).

[7] Bogert and Updike, THIS JOURNAL, **49**, 1373 (1927).

[8] Bogert and Taylor, *Collection Czechoslov. Chem. Communications*, **3**, 480 (1931).

The reaction flask (A) was kept warm (50°) and 1.1 cc. of freshly distilled benzaldehyde was run in through the funnel tube. The hydrogen sulfide inlet and all outlets were closed and the zinc sulfide was allowed to settle. The supernatant liquid was siphoned over into flask B and then some distilled water from C was siphoned over into it. After standing for twenty-four hours, with all outlets closed, clusters of needles crystallized from the mixture in B. Recrystallized from alcohol, yellowish needles were obtained contaminated with some resinous material. When this resin was removed by washing with ether, the crystals became colorless, melted at 113–114°, and proved to be 2-phenylbenzothiazole. Evaporation of the ether extract left a hard foul-smelling resin, which could not be crystallized from alcohol, ether, benzene, glacial acetic acid or acetic anhydride, liquefied at 80–90°, and was probably a thiobenzaldehyde produced by the action of the hydrogen sulfide upon the benzaldehyde.

In another series of experiments the formation of these undesirable sulfur compounds was avoided by precipitating the zinc first, filtering from the zinc sulfide and using the glacial acetic acid filtrate, containing the *o*-aminothiophenol in solution, in the same apparatus in an atmosphere of hydrogen in place of hydrogen sulfide. Recently boiled water was siphoned into the flask, after the completion of the benzaldehyde reaction, and all outlets were closed. After standing for some time (twenty-four hours), brown crystals separated, m. p. 104–106°. Recrystallized twice from alcohol, colorless needles, m. p. 114°, were obtained, which proved to be 2-phenylbenzothiazole.

To prove that the crude product (m. p. 104–106°) was not a benzothiazoline, acetic anhydride was added after the benzaldehyde, to acetylate the —NH group if present, but again the only product isolated was the 2-phenylbenzothiazole.

(3) In a third series, zinc *o*-aminothiophenolate (1 g.) was suspended in warm glacial acetic acid (50 cc.), benzaldehyde (1 g.) added and a rapid stream of hydrogen sulfide passed through the mixture until all zinc had been precipitated as sulfide. The filtrate from this precipitate when diluted with 4–5 volumes of water separated 2-phenylbenzothiazole. The filtrate from this thiazole was distilled. After a considerable portion of the liquid had passed over at about 100°, more of the 2-phenylbenzothiazole separated and was removed, and the distillation was continued with the filtrate, which went over at 102–120°, leaving a small amount of partially charred residue. The total yield of 2-phenylbenzothiazole was 60–65%.

In none of these sets of experiments did we detect any liberation of hydrogen, or succeed in isolating any benzothiazoline. Nor did we find any evidence of the formation of reduction products of the benzaldehyde, although we searched the various reaction products for benzyl alcohol, hydrobenzoin, stilbene, etc.

Zinc *o*-Benzalaminothiophenolate, $(C_6H_5CH{=}NC_6H_4S{-})_2Zn$.—A mixture of 2 g. of zinc *o*-aminothiophenolate with 6 cc. of freshly distilled benzaldehyde was boiled for three minutes. The colorless zinc thiophenolate dissolved rapidly to a deep red solution which, as it cooled, separated red crystals. These crystals were collected, washed thoroughly with small quantities of cold benzene and dried; yield, 2.5 g., or about 80%. These crystals were practically insoluble in water, and only slightly soluble in benzene, toluene or xylene. Recrystallized from benzene, in a modified Soxhlet extractor, the compound was obtained in reddish-orange plates, m. p. 230–232° (corr.), and the yield was thereby reduced to 35–40%. Qualitative tests showed the presence of nitrogen and sulfur. This extraction was necessary in order to separate the anil from the zinc salt; but the longer the boiling was continued the more 2-phenylbenzothiazole was formed.

Anal. Calcd. for $C_{26}H_{20}N_2S_2Zn$: C, 63.72; H, 4.12; ZnO, 16.62. Found: C, 63.58; H, 4.25; ZnO, 16.81, 16.49, 16.58.

These crystals when heated in the air or in an atmosphere of hydrogen, melted first to a deep red liquid. At 140–160° and 1.5 to 2 mm. pressure, some of this material distilled over and congealed in the receiver to a red solid. There was formed also a white sublimate of 2-phenylbenzothiazole. The black tarry residue remaining in the distilling flask yielded ZnO when ignited. The red congealed distillate proved to be a mixture of 2-phenylbenzothiazole and unchanged initial zinc benzalaminothiophenolate.

Refluxed for five minutes with glacial acetic acid (20 cc.), these red crystals (1 g.) dissolved to a colorless solution, from which 0.33 g. of zinc acetate crystallized, accounting for 89% of the zinc in the initial compound. By addition of two volumes of water to the mixture, the zinc acetate was re-dissolved, the solution became turbid and after standing for an hour 0.76 g. of curdy yellow solid precipitated which, when decolorized and crystallized from alcohol, yielded 0.52 g. of 2-phenylbenzothiazole, or 64% of that calculated.

When the benzaldehyde was added to a suspension of the zinc *o*-aminothiophenolate in boiling glacial acetic acid, a nearly clear yellowish solution was formed almost immediately, from which the 2-phenylbenzothiazole was isolated either as described in the foregoing paragraph, or by saturating the acetic acid solution with hydrogen sulfide, filtering out the zinc sulfide, and diluting the filtrate.

Even refluxing the zinc *o*-benzalaminothiophenolate with 95% alcohol for six hours converted a considerable amount (0.287 g. from 1.74 g. of zinc salt) into the 2-phenylbenzothiazole. There was formed at the same time a yellow precipitate, containing zinc, nitrogen and sulfur, which was unmelted at 255° (corr.) and when ignited decomposed with a strong odor of 2-phenylbenzothiazole and left a zinc oxide ash. Digested with alcohol or with benzene, this yellow precipitate was unaltered, but when it was suspended in a 1:1 mixture of concentrated ammonium hydroxide and water, and air was bubbled through for two hours, some *o*-aminophenyl disulfide was formed (m. p. 93° corr.).

The zinc benzalaminothiophenolate itself, when suspended in dilute ammonium hydroxide and similarly treated, was practically unaffected and 85% was recovered without difficulty.

All attempts to oxidize the zinc benzalaminothiophenolate, due to its insolubility, either were without apparent effect or yielded 2-phenylbenzothiazole. Our experiments for the preparation of the corresponding sodium benzalaminothiophenolate were unsuccessful.

Boiling the zinc benzalaminothiophenolate with ether or with acetone changed it, in the same manner as boiling with alcohol, to the thiazole, although the change proceeded more slowly.

Similar zinc anil salts were prepared in the same way by the action of zinc *o*-aminothiophenolate upon salicylaldehyde, piperonal and alpha-fural, and are given in the subjoined table. All of these products gave qualitative reactions for zinc, nitrogen and sulfur.

TABLE I

ZINC SALTS OF ANILS FROM *o*-AMINOTHIOPHENOL

Aldehyde	Salicyl	Piperonal	α-Fural
Crystals	Yellow	Yellow	Red
Yield, %	65	70	*ca.* 100
Dec., °C.	250	245–250	232–240
ZnO calcd.	15.60	14.09	17.33
ZnO found	15.83	14.16	17.34 17.55

These anil zinc salts were converted into the corresponding 2-R-benzothiazoles by refluxing for ten minutes with glacial acetic acid and then diluting. The results are summarized in Table II.

TABLE II

2-R-BENZOTHIAZOLES FROM ANIL ZINC SALTS

The yields given in this table are for the purified and recrystallized products.

Initial anil	Salicyl	Piperonal	α-Fural
Benzothiazole prod.	2-(*o*-Hydroxyphenyl)[a]	2-(*m*,*p*-Methylenedioxyphenyl)-[b]	2-(α-Furyl)-[c]
Colorless	Crystals	Scales	Flakes
Yield, %	29	52	33
M. p., °C. corr.	130	125	104.5

[a] Bogert and Corbitt[3] give the m. p. as 131.1–131.7° (corr.). [b] Bogert and Stull[8] give the m. p. as 125° (corr.). [c] Bogert and Stull[8] give the m. p. as 105° (corr.).

Like the analogous benzal derivative, the zinc *o*-furalaminothiophenolate when refluxed with 95% alcohol suffered decomposition with production of the 2-(α-furyl)-benzothiazole and formation of a yellow precipitate containing zinc (ZnO, 35.09%), nitrogen and sulfur.

II. The Action of *o*-Aminophenyl Disulfide with Aldehydes

***o*-Aminophenyl Disulfide and Benzaldehyde.**—When a mixture of the disulfide and benzaldehyde was heated at 130° for an hour, or refluxed for only five minutes, 2-phenylbenzothiazole was the only pure product isolated; yield, 0.29 g. of crude material from 0.2 g. of the disulfide and 0.25 cc. of benzaldehyde. No benzal derivative of the aminodisulfide was encountered.

Similarly, when a solution of 1 g. of the disulfide in 2 cc. of hot xylene, with 0.3 cc. of benzaldehyde added, was refluxed for an hour, the product was again the 2-phenyl benzothiazole, yield 71%. In the presence of a lower boiling solvent, however, the intermediate benzal derivative was obtained.

***o*-Benzalaminophenyl Disulfide,** $(C_6H_5CH{=}NC_6H_4S{-})_2$.—To a solution of 1 g. of the disulfide in 10 cc. of alcohol, there was added 0.82 cc. of benzaldehyde and the mixture was refluxed for ten minutes. As the solution cooled, a yellow oil and a few long yellow crystals precipitated. The mixture of oil and crystals was purified by crystallization from alcohol and there was thus obtained 1.4 g. (or 82%) of yellow needles which, after recrystallization from alcohol, melted at 138.5–139.5° (corr.), and were easily soluble in ether or benzene, but dissolved only slightly in alcohol. By diluting their hot benzene solution with hot alcohol and cooling slowly, large yellow needles or hexagonal plates were obtained, m. p. 140° (corr.).

Anal. Calcd. for $C_{26}H_{20}N_2S_2$: C, 73.53; H, 4.75; S, 15.11; N, 6.53. Found: C, 73.63; H, 5.02; S, 15.01; N, 6.69.

This anil was readily hydrolyzed to the aminophenyl disulfide (m. p. 93°) and benzaldehyde again when boiled with glacial acetic acid, or refluxed for at least thirty minutes with dilute alcohol; whereas similar treatment of the zinc salts of the *o*-aminothiophenol anils gave the benzothiazole, as noted above.

When a mixture of 0.5 g. of this anil, with or without 2 cc. of xylene, and 0.26 cc. of benzaldehyde was refluxed for an hour, 2-phenylbenzothiazole was produced in large amount.

Attempts to reduce an alcoholic solution of the anil with either sodium or sodium amalgam proved futile.

Analogous results were obtained with salicylic aldehyde and with fural, as follows.

***o*-Salicylaminophenyl disulfide:** yellow needles (from benzene), m. p. 171° (corr.); yield, 52%; S calcd. 14.04; S found, 13.81.

***o*-α-Furalaminophenyl disulfide:** pale yellowish needles (from alcohol), m. p. 134.5° (corr.); yield, 25%; S calcd., 15.86; S found, 15.79 and 15.67.

Each of these, when mixed with about an equal weight of its initial aldehyde and refluxed, direct or in xylene solution, gave the corresponding 2-R-benzothiazole in large yield.

III. The Action of 4-Chloro-2-aminothiophenol with Aldehydes

With the work of Lankelma and Sharnoff[4] before us, suggesting that the halogenated 2-phenylbenzothiazolines were probably more stable than the unhalogenated ones, we carried out a parallel series of experiments with the zinc 4-chloro-2-aminothiophenolate. This was prepared by reducing a glacial acetic acid solution of the 4-chloro-2-nitrophenyl disulfide with zinc dust, essentially as described by Bogert and Snell[9] for the zinc *o*-aminothiophenolate; yield, 89%.

Zinc 4-Chloro-2-benzalaminothiophenolate, $(C_6H_5CH{=}NC_6H_3(Cl)S)_2Zn$, prepared by boiling for about five minutes a mixture of the zinc chloroaminothiophenolate and benzaldehyde, crystallized from xylene in red plates, m. p. 207–208° (corr.); yield, 29%.

Anal. Calcd. for $C_{26}H_{18}N_2S_2Cl_2Zn$: ZnO, 14.57; found, 14.70.

Qualitative tests showed the presence also of nitrogen, sulfur and chlorine.

The duration of the heating of the mixture of zinc salt and benzaldehyde is important. It should continue only until a clear red solution is obtained. For the chlorinated zinc salt this means generally about two minutes, for the unchlorinated salt, less than one minute. In either case, longer heating changes all to the corresponding benzothiazole.

---

[9] Bogert and Snell, THIS JOURNAL, **46**, 1309 (1924).

5-Chloro-2-phenylbenzothiazole.—When the above benzal derivative was refluxed in glacial acetic acid solution and the product separated as described in the similar cases above, the only pure compound isolated was the 5-chloro-2-phenylbenzothiazole, m. p. 138.5–139° (corr.), whose properties coincided entirely with those ascribed to this compound by Lankelma and Knauf;[10] yield, 52%.

The first crude product which separated in this reaction melted at 127–130°, and its melting point was raised to 138.5–139° (corr.) by crystallization from a mixture of petroleum ether and ether. Lankelma and Sharnoff[4] give the melting point of 5-chloro-2-phenylbenzothiazoline as 127°, so that even this crude product must have been mainly the thiazole.

When refluxed for four hours with alcohol, the zinc benzalamino derivative gave a 55% yield of the thiazole. Even refluxing with petroleum ether slowly converted the zinc benzalamino derivative into the thiazole, although the quantity formed, even after twelve hours of heating, was but small.

Summary

1. It is shown that anils are intermediate products in the formation of benzothiazoles from aromatic aldehydes and *o*-aminothiophenol.

2. Zinc *o*-aminothiophenolate can be condensed directly with aromatic aldehydes to crystalline bright-colored anil zinc salts of the general formula $(RCH{=}NC_6H_4S)_2Zn$, which yield 2-R-benzothiazoles when boiled for a few minutes in glacial acetic acid solution.

3. *o*-Aminophenyl disulfide likewise forms anils with aromatic aldehydes. These anils yield the 2-R-benzothiazoles readily when mixed with their parent aldehyde and refluxed in xylene solution.

4. Analogous results are recorded using 4-chloro-2-aminothiophenol as initial material.

NEW YORK, N. Y. RECEIVED JUNE 4, 1935

---

[10] Lankelma and Knauf, THIS JOURNAL, **53**, 311 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

Sulfonation of Acridone

BY KONOMU MATSUMURA

Concerning the formation of acridones by the dehydration of phenylanthranilic acid and its derivatives with sulfuric acid,[1] a search of the literature reveals that on prolonged heating certain substituted phenylanthranilic acids give a low yield of the desired acridone.[2] Since no statement is recorded regarding the other reaction products, it appeared desirable to examine this reaction further.

In the present paper it is reported that acridone is best prepared by heating a solution of phenylanthranilic acid in concentrated sulfuric acid at 85° for one-half hour and that on further heating sulfonation occurs. Results are summarized in the tables.

TABLE I

REACTION BETWEEN PHENYLANTHRANILIC ACID AND CONCENTRATED SULFURIC ACID

Subs., g.	15	15	15	30
H_2SO_4, g.	150	150	150	450
Reaction time, min.	30	45	90	120
Temp., °C.	85	85	100	100
Acridone, g.	13.5	11.8	4.8	0.05
Acridone-2-sulfonic acid, g.			11.5	39.3
Acridone-4-sulfonic acid, g.				0.9

Evidence that the sulfonic acid of m. p. 318° isolated predominantly may be acridone-2-sulfonic acid and the other sulfonic acid of m. p. 268° isolated in a minute amount may be acridone-4-sulfonic acid, was obtained in the following way. The attempted condensation of sulfanilic acid with *o*-chlorobenzoic acid either in amyl alcohol or in aqueous solution failed and hence direct identification by a synthetic method which leaves no doubt as to the constitutions was not attained. Therefore application of alkali fusion, which is reliable on the basis of the assumption that group migration does not occur during the reaction, was adopted as a method of establishing orientation. On fusion with alkali, the sulfonic acid of m. p. 318° was found to give 2-hydroxyacridone and the sulfonic acid m. p. 268° to give 4-hydroxyacridone, respectively, both hydroxyacridones being identified by comparison with authentic specimens of synthetic material. Therefore, in acridone, sulfonation appears to follow the same course as does nitration.[3]

With the use of acridone-2-sulfonic acid as starting material, diacridyl-2,2′-disulfide (I) could be made while attempts to prepare 9-aminoacridine-2-sulfonic acid failed. 9-Chloroacridine-

---

[1] Graebe and Lagodzinski, *Ber.*, **25**, 1734 (1892).

[2] Ullmann, *Ann.*, **355**, 312 (1907); Matsumura, THIS JOURNAL, **49**, 813 (1927).

[3] Lehmstedt, *Ber.*, **64**, 2381 (1931).