[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

RESEARCHES ON THIAZINES. I. SYNTHESES IN THE PERI-NAPHTHO-META-THIAZINE GROUP

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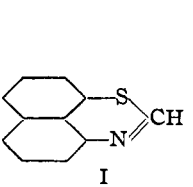
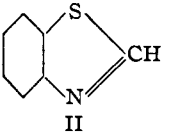
The investigations which our laboratory has been conducting during recent years on benzothiazoles, have led us to take up also the study of certain *m*-thiazines whose structure is somewhat analogous. Thus, the structural relationship of *peri*-naphtho-*m*-thiazine (I) to benzothiazole (II) is similar to that of naphthalimide (III) to phthalimide (IV)



I



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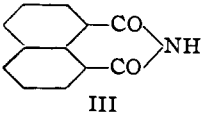
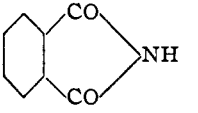
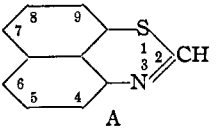


III



IV

The *peri*-position of the naphthalene nucleus resembles in so many ways the *o*-position of the benzene nucleus, that it seemed to us of interest to ascertain whether or not synthetic methods found serviceable in the benzothiazole field could be utilized for the preparation of *peri*-naphthothiazines, and to what extent the properties of the latter class of compounds would resemble those of the former. As expected, the results have shown that, both in methods of preparation and in properties, the two groups resemble each other closely, and this applies also to the tinctorial properties of analogously constituted dyes in the two series.



A

The numbering of the *peri*-naphthothiazine nucleus used in this article is shown in (A).

The only *peri*-naphthothiazine we have found in the literature is the 2-phenyl derivative, which Reissert[1] obtained by the action of alcoholic alkali upon the dibenzoyl derivative of 1,8-aminonaphthyl mercaptan.

The syntheses we carried out were briefly as follows.

Sodium 1-naphthalene sulfonate was converted into its sulfochloride, which was then nitrated. The 1,8-nitrosulfochloride was separated from its 1,5-isomer and reduced in acetic acid solution with stannous chloride and dry hydrogen chloride to a chlorostannate (V) of the *peri*-aminonaphthyl mercaptan and a tin chloride addition product (VI) of a mono-acetylated *peri*-aminonaphthyl mercaptan. These complex tin compounds easily

[1] Reissert, *Ber.*, 55, 858 (1922).

yielded both di-acyl derivatives of the *peri*-aminomercaptan and the corresponding thiazines when dissolved in glacial acetic acid and treated with acyl chlorides in the presence of fused sodium acetate. We believe that this indirect method of preparing acyl derivatives of amines may prove of service in other cases where the free amine itself is unstable or difficult to isolate. Kehrmann, Oulevay and Regis[2] record the preparation of some acylated amines by the action of acetic anhydride and sodium acetate upon the chlorostannates of amines; while Jacobs and Heidelberger[3] found that amines could be acylated conveniently by the action of acyl halide upon an aqueous acetic acid solution of the amine in the presence of sodium acetate.

From the acyl derivatives of the *peri*-aminomercaptan, or directly from their antecedent complex tin compounds, the 2-R-*peri*-naphthothiazines were obtained readily, the cyclization being effected by alcoholic sodium hydroxide solution or, better, by digesting in glacial acetic acid solution with sodium acetate. The naphthothiazines thus synthesized were the 2-methyl and 2-(*o*-, *m*- and *p*-)-nitrophenyl. Reduction of the nitrophenyl derivatives yielded the corresponding aminophenyl compounds, from which in turn hydroxy derivatives were prepared by the usual diazo reaction, or dyes of Chloramine Yellow (Colour Index No. 814) type by sulfonation followed by hypochlorite oxidation.

The reactivity of the methyl group in the 2-methyl derivative was demonstrated by condensing it with benzaldehyde and with phthalic anhydride, obtaining in the former case the 2-styryl derivative, and in the latter the quinophthalone or Quinoline Yellow (Colour Index No. 801) analog.

These various steps and products are shown on the Flow Sheet.

For convenience and brevity in what follows, the compound represented by Formula (V) on that Flow Sheet will be designated the "chlorostannate," and compound (VI) as the "tin chloride addition product," although we have not succeeded in definitely establishing the constitution of either one.

By the action of the nitrobenzoyl chlorides (*m*- and *p*-) upon the tin chloride addition product, the acetyl group was displaced and a di-nitrobenzoyl derivative (X) formed. The solubility of the diacylated aminomercaptans (X and XVII) in the ordinary organic solvents was less than that of the thiazines resulting therefrom by cyclization. This *peri*-thiazine cyclization was accompanied by color formation, the colorless, or only faintly colored, acylamino mercaptans changing to the deeply colored thiazines. This production of color may be peculiar to the *peri*-position, or the *m*-thiazine nucleus itself may be chromophoric intrinsically.

In so far as the influence of substituents was concerned in the case of isomeric thiazines, there was a greater color difference between the *o*-,

[2] Kehrmann, Oulevay and Regis, *Ber.*, **46**, 3712 (1913).

[3] Jacobs and Heidelberger, THIS JOURNAL, **39**, 1439 (1917).

FLOW SHEET

C10H7SO3Na (1)
C10H7SO2Cl
C10H6(SO2Cl (1), NO2 (8))
(?) [C10H6(SH (1), NH2 (8))]2 V
SnCl4
(?)
C10H6(SH (1), NHAc (8)) VI
SnCl4
C10H6(S, N, CCH3) VII
C10H6(S, N, CCH=CHC6H5) VIII
C10H6(S, N, CCH(CO, CO)C6H4) IX
Dye
C10H6(SCOC6H4NO2(m, or p), NHCOC6H4NO2(m, or p)) X
C10H6(S, N, CC6H4NO2(m, or p)) XI
Dye
C10H6(S, N, CC6H4NH2) XII
C10H6(S, N, CC6H4OH) XIII
C10H6(SH, NHCOC6H4NO2(o-)(?)) XIV
C10H6(S, N, CC6H4NO2 (o-)) XV
C10H6(S, N, CC6H4NH2(o-)) XVI
C10H6(SCOC6H4NO2 (o-), NHCOC6H4NO2 (o-)) XVII

m- and *p*-nitrophenyl isomers than between the aminophenyl or hydroxyphenyl isomers. In the case of the *o*-nitrobenzoyl derivative (XVII), it was found that reduction and cyclization could be effected in one operation, with production of the 2-aminophenyl thiazine (XVI). In the cyclization of the nitrobenzoyl derivatives, the *o*-nitro closed up much more slowly and with more difficulty than either the *m*- or *p*-isomers. Similarly, the sulfonation of the 2-aminophenyl thiazines (XII and XVI) proceeded more slowly with the *o*- than with the *m*- or *p*-isomers, but all three isomers sulfonated more rapidly and at lower temperature than dehydrothio-*p*-toluidine.

The dye of Quinoline Yellow type prepared from the 2-methyl naphthothiazine dyed wool a somewhat darker yellow than Quinoline Yellow itself, but in fastness to light, laundering, bleeding, etc., the two were indistinguishable.

The Chloramine Yellow type of dyes, prepared from the 2-aminophenyl derivatives (XII), both dyed cotton directly. That from the *p*-amino compound gave a burgundy shade, which compared well with Chloramine Yellow itself in fastness to light, etc. The *m*-amino isomer dyed cotton a tan, which was less fast to light, etc. The sodium sulfonate of the 2-*o*-aminophenyl derivative (XVI) was too difficultly soluble to be converted into the dye conveniently.

Cyanines are now being prepared from the 2-methyl derivative, in order to test their photosensitizing effects; and the investigation is being continued and extended in other directions also.

Experimental Part

1-Naphthalenesulfochloride, $C_{10}H_7SO_2Cl$.—A technical grade of sodium 1-naphthalenesulfonate, obtained from the General Dyestuff Corporation, New York, N. Y., was converted into the sulfochloride by utilization of the methods of Erdmann and Süvern[4] and of Bourgeois,[5] with a few minor modifications.

1,8-Nitronaphthalene Sulfochloride, $C_{10}H_6(NO_2)SO_2Cl$.—In our early experiments for the production of this nitrosulfochloride, a crude mixture of the calcium salts of the 1,5- and 1,8-nitronaphthalene sulfo acids was used. This was supplied through the generosity of the National Aniline and Chemical Co., Inc., New York, N. Y., to whom we wish to express our grateful acknowledgment. The labor and time required to prepare from this crude material, in satisfactory yield and purity, the compound sought, were so great that we were forced to return to 1-naphthalenesulfochloride as our starting point, which was then nitrated by a modification of the processes of Erdmann and Süvern[4] and of Reissert.[1]

Peri-aminonaphthyl Mercaptan Chlorostannate (V).—Reduction of the nitrosulfochloride to the amino mercaptan was attempted by the method of Reissert,[1] which involves the isolation first of the aminosulfinic acid. This proved unsatisfactory, because of the large quantities of ferric hydroxide to be filtered, the instability of the product and the variation in yields.

[4] Erdmann and Süvern, *Ann.*, **275**, 233 (1893).

[5] Bourgeois, *Rec. trav. chim.*, **18**, 439 (1899).

Experiments showed, however, that the nitrosulfochloride could be reduced directly to the desired aminomercaptan by the action of a glacial acetic acid solution of stannous chloride saturated with dry hydrogen chloride. There was thus obtained, not the free aminomercaptan, but two complex tin derivatives thereof which answered our purposes equally well. Both were separated in imperfect crystalline form. Their analyses, although decidedly inconclusive and unsatisfactory, suggested that one (V) was probably a chlorostannate of the aminomercaptan, while the figures for the other (VI) indicated a tin chloride addition product of the monoacetylated aminomercaptan. It is possible that the former of these was identical with the product separated by Reissert,[1] although his compound was different in color and was not analyzed.

The chlorostannate was prepared as follows.

A mixture of 65 g. of $SnCl_2 \cdot 2H_2O$ with 210 g. of glacial acetic acid was brought into solution by passing in dry hydrogen chloride until the gain in the weight of the mixture amounted to 26 g. To this solution 10 g. of the nitrosulfochloride was added all at once and the mixture shaken vigorously. Reduction ensued immediately, and the nitrosulfochloride dissolved, with rise in the temperature of the solution to 80–85°. Solution had scarcely occurred, however, before the chlorostannate separated in irregular gray crystals. When cooled to room temperature, the precipitate was collected, washed with glacial acetic acid, then with benzene and finally with ether; yield, 10 g., or 79% if calculated to Formula (V).

Anal. Calcd. for $C_{20}H_{20}N_2S_2SnCl_6$: C, 35.10; H, 2.95; Sn. 17.36; Cl, 31.11. Found: C, 35.92; H, 3.79; Sn, 17.0; Cl, 27.4.

On long standing in the air, or in contact with water or alcohol, it changed to a yellow product. It was insoluble in the ordinary solvents, but dissolved in a hot mixture of equal volumes of concentrated hydrochloric and glacial acetic acids, but such a mixture could not be used for crystallization, since heating of this solution transformed the chlorostannate into the tin chloride addition product described in the next paragraph.

Tin Chloride Addition Product of *Peri*-acetaminonaphthyl Mercaptan (VI).—This was prepared most conveniently from the chlorostannate as formed in the reaction just described.

In that reaction, as soon as the chlorostannate began to separate, the mixture was heated under a reflux (six or seven minutes) until all was once more in solution. When this solution cooled, an orange-yellow crystalline precipitate separated, which was collected, washed with a small amount of water, then with glacial acetic acid and finally with ether and dried; yield, 12 g. from 10 g. of the nitrosulfochloride, or 57%, if calculated to Formula (VI).

Anal. Calcd. for $C_{12}H_{11}ONS \cdot SnCl_4$: C, 30.15; H, 2.32; Sn, 24.85; Cl, 29.69. Found: C, 31.84; H, 2.46; Sn, 25.5; Cl, 29.1.

The product was slightly soluble in water, alcohol, glacial acetic or concentrated hydrochloric acid, but these solvents were unsuitable for crystallization because either ring closure or decomposition resulted on heating. On standing exposed to the air, or in contact with water or with alcohol, it was much more stable than the chlorostannate. Its color was also of interest. The presence of an acetyl group was demonstrated by the fact that it gave the methylthiazine when treated with alcoholic sodium hydroxide, whereas no thiazine could be obtained by similar treatment of the chlorostannate.

2-Methyl-*peri*-naphthothiazine (VII).—A solution of 9 g. of fused sodium acetate in 90 cc. of glacial acetic acid was heated nearly to its boiling point, 9 g. of the tin chloride addition product dropped in and the mixture agitated vigorously. A dull orange solution resulted, with simultaneous precipitation of sodium chloride. While the mixture

was still hot (about 95°), 13 g. of acetic anhydride was added in three separate portions. The mixture was shaken well, allowed to cool, poured into water, the yellow flocculent precipitate collected and crystallized from 60% alcohol in the presence of norite. Yellow needles were obtained, m. p. 96.5–97.5° (corr.); yield, 3.5 g., or 93%.

Anal. Calcd. for $C_{12}H_9NS$: C, 72.31; H, 4.56; N, 7.03. Found: C, 72.38; H, 4.66; N, 6.68.

It was soluble in alcohol, ether, acetic acid, ethyl acetate, benzene or chloroform. In concentrated hydrochloric or sulfuric acid, it dissolved to dark yellow solutions, from which it was not reprecipitated by dilution.

The same compound was obtained from the tin chloride addition product without the use of acetylating agents. A suspension of 2 g. of the addition product in 50 cc. of alcohol was treated with sufficient 10% sodium hydroxide to bring all into solution. After it had stood for an hour, this solution was diluted with water to turbidity and, on longer standing, the methyl thiazine separated in yellow needles which when recrystallized from dilute alcohol showed the same m. p. (96.5–97.5°) as the first preparation, and this m. p. was the same for an intimate mixture of the two. The yield by this second method, however, was only 15% (0.125 g.).

2-Styryl-*peri*-naphthothiazine (VIII).—To a solution of 2 g. of the methylthiazine and 1.3 g. of benzaldehyde in 35 cc. of alcohol, there was added 10 cc. of a 10% sodium hydroxide solution and the mixture was allowed to stand at room temperature for thirty-six hours. The orange-red needles which separated were collected and dried. They amounted to 1.3 g. (45% yield) and melted at 128–129°. Recrystallization from alcohol, in the presence of norite, raised the m. p. to 132–133° (corr.).

Anal. Calcd. for $C_{19}H_{13}NS$: C, 79.39; H, 4.56. Found: C, 79.55; H, 4.92.

The compound was soluble in alcohol, ether, glacial acetic acid, ethyl acetate, benzene or chloroform. Concentrated hydrochloric acid changed the color of the needles to purple, but failed to dissolve them. Concentrated sulfuric acid dissolved the compound to a red solution, from which it was reprecipitated by dilution.

2-Methyl-*peri*-naphthothiazine Phthalone (IX).—An intimate mixture of 2 g. of the methyl thiazine, 1.7 g. of phthalic anhydride and 3 g. of zinc chloride was heated at 190–200° for two and a half hours. The cooled and pulverized melt was extracted first with dilute hydrochloric acid, then with alcohol, after which the residue was dissolved in glacial acetic acid, boiled with norite, filtered hot and the filtrate diluted with water. The flocculent yellow precipitate obtained crystallized from glacial acetic acid as a pale brown practically amorphous powder, m. p. 173.5–174.5° (corr.); yield, 0.9 g., or 27%.

Anal. Calcd. for $C_{20}H_{11}O_2NS$: C, 72.91; H, 3.37. Found: C, 72.53; H, 3.66.

It was practically insoluble in alcohol, ether, sodium hydroxide solution or in concentrated hydrochloric acid; but dissolved in chloroform, benzene or glacial acetic acid. In concentrated sulfuric acid, it dissolved to a red solution, from which it was reprecipitated unchanged by dilution.

An Analog of Quinoline Yellow Dye.—A solution of 1 g. of the above phthalone in 5 cc. of concentrated sulfuric acid, after standing for an hour at room temperature, was poured upon ice, the separated sulfo acid collected, redissolved in water, the solution neutralized with sodium hydroxide and the sodium sulfonate precipitated by the addition of a saturated sodium chloride solution. The precipitate dried to a pale brown solid, insoluble in alcohol or in concentrated sodium hydroxide solution, but which dissolved in concentrated sulfuric acid to a red solution.

Comparative dye tests were carried out with commercial Quinoline Yellow as follows:

Wool (nun's veiling), 3.0 g.
Dye, 90 cc. of 0.067% solution (0.06 g. of dye)
$Na_2SO_4 \cdot 10H_2O$, 0.5 g.
H_2SO_4 concd., 0.1 g.

The previously moistened wool was entered in the lukewarm dye-bath, the mixture heated to boiling and kept there for forty-five minutes.

The shade produced by the new dye was a bright yellow, rather darker than that obtained with Quinoline Yellow. In fastness to light, laundering and bleeding, there was no appreciable difference between the two.

Di-(*o*-Nitrobenzoyl)-*peri*-aminonaphthyl Mercaptan (XVII).—Ten grams of the chlorostannate was decomposed in 100 cc. of hot glacial acetic acid containing 10 g. of fused sodium acetate, in the same way that the tin chloride addition product was used for the preparation of the methylthiazine, except that the decomposition of the chlorostannate proceeded somewhat more slowly than with the addition product. However, solution occurred with simultaneous precipitation of most of the chlorine as sodium chloride. After the mixture had cooled to about 20°, 11 g. of *o*-nitrobenzoyl chloride was added with vigorous shaking and it was left overnight at room temperature. The gray precipitate was collected, washed thoroughly with water and dried. It amounted to 6.9 g., melted at about 170°, and proved to be the crude di-(*o*-nitrobenzoyl)-aminomercaptan. The mother liquor from this crude di-acyl derivative contained the corresponding thiazine, as noted below.

The crude di-acyl derivative was recrystallized from glacial acetic acid (200 cc.), in the presence of norite, and yielded 2.1 g. of pale brown prismatic needles. In the mother liquor there remained the mono-acyl derivative, as described beyond. The di-acyl derivative was further purified by crystallization from benzene, and then melted with decomposition at about 185.5–186.5° (corr.), this decomposition point varying depending upon rate of heating. On standing exposed to light and air, it gradually darkened in color.

Anal. Calcd. for $C_{24}H_{15}O_6N_3S$: C, 60.86; H, 3.20. Found: C, 60.80; H, 3.56.

It dissolved slightly in alcohol, chloroform, benzene or ethyl acetate, and more freely in glacial acetic acid. In sodium hydroxide solution, or in concentrated hydrochloric acid, it was practically insoluble but dissolved in concentrated sulfuric acid to a red solution from which it was re-precipitated by dilution.

Mono-(*o*-nitrobenzoyl)-*peri*-aminonaphthyl Mercaptan (XVI).—The glacial acetic (200 cc.) mother liquor from the recrystallization of the crude di-(*o*-nitrobenzoyl)-aminomercaptan, when diluted with water, separated a flocculent orange-yellow precipitate. This was removed, extracted with alcohol to remove any thiazine which might be present and then crystallized from glacial acetic acid. The yellowish gray solid so obtained was practically amorphous and melted with decomposition at about 225°; yield, 1.3 g. Further purification by crystallization from xylene did not alter this decomposition point appreciably.

Anal. Calcd. for $C_{17}H_{12}O_3N_2S$: C, 62.93; H, 3.73. Found: C, 63.24; H, 3.41.

It dissolved slightly in xylene or in glacial acetic acid, but was practically insoluble in sodium hydroxide solution or in concentrated hydrochloric acid. In concentrated sulfuric acid it dissolved to a pale yellow solution, from which it was reprecipitated by dilution.

Di-(*m*-nitrobenzoyl)-*peri*-aminonaphthyl Mercaptan (X).—The tin chloride addition product (5 g.) was decomposed by a hot glacial acetic acid solution (100 cc.) of fused sodium acetate (5 g.), the mixture then cooled to about 20°, 5.5 g. of *m*-nitrobenzoyl chloride added all at once and the mixture agitated vigorously, while keeping the tem-

perature at about 20°. After standing for two hours longer, the buff-colored precipitate which had separated was removed, washed thoroughly with water and crystallized from benzene, in the presence of norite. Colorless silky needles were thus secured, which melted with decomposition at about 210–213° (corr.); yield, 2.8 g., or 57%. On exposure to the light, they slowly darkened.

Anal. Calcd. for $C_{24}H_{15}O_6N_3S$: C, 60.86; H, 3.20. Found: C, 61.07; H, 3.35.

It was soluble in chloroform, benzene, glacial acetic acid or ethyl acetate, practically insoluble in sodium hydroxide solution or in concentrated hydrochloric acid, but dissolved in concentrated sulfuric acid to a colorless solution from which it separated again on dilution.

Instead of the tin chloride addition product, it was found that the chlorostannate could be used, but the di-acyl derivative so obtained was less pure.

Di-(*p*-nitrobenzoyl)-*peri*-aminonaphthyl mercaptan (X) was prepared in essentially the same manner as its *m*-isomer, from 5 g. of the tin chloride addition product, 150 cc. of hot glacial acetic acid, 7.5 g. of fused sodium acetate and 5 g. of the acyl chloride added at about 75°. An orange precipitate began to separate almost immediately. When the mixture had cooled to about 40°, the precipitate was removed, washed thoroughly with water and crystallized from glacial acetic acid, in the presence of norite. The microscopic canary yellow needles so obtained melted with decomposition at about 248–249° (corr.); yield, 2.95 g., or 60%.

Anal. Calcd. for $C_{24}H_{15}O_6N_3S$: C, 60.86; H, 3.20. Found: C, 61.10; H, 3.24.

The product was insoluble in alcohol, ether, benzene, chloroform, ethyl acetate, sodium hydroxide solution or concentrated hydrochloric acid, and but slightly soluble in glacial acetic acid. It dissolved in concentrated sulfuric acid to a pale yellow solution and was reprecipitated therefrom by dilution.

The filtrate from the first precipitate of the crude dinitrobenzoyl derivative, when poured into water, separated a red flocculent precipitate which, on crystallization from glacial acetic acid, yielded 0.4 g. of 2-(*p*-nitrophenyl)-*peri*-naphthothiazine, m. p. 208–209° (corr.), identical with that described beyond.

As in the case of the *m*-isomer, this same di-acyl aminomercaptan was prepared from the chlorostannate also but, as was true for the *m*-isomer, the product was less pure than when the tin chloride addition compound was employed.

Reissert[1] obtained the dibenzoyl-*peri*-aminonaphthyl mercaptan by decomposing the chlorostannate with sodium hydroxide solution and then adding benzoyl chloride, but he did not report his yield. An attempt was made to repeat his process, using *p*-nitrobenzoyl in place of benzoyl chloride, but the results were very unsatisfactory, even when the chloride was used in ether or benzene solution. The acylation was also tried in the presence of pyridine, according to the method of Heller and Nötzel,[6] but the results were equally poor.

The tin chloride addition product was next studied, in the hope that it might be possible to use it directly for acylation, and the results obtained in this study with *p*-nitrobenzoyl chloride blazed the trail which was followed for the preparation of the other compounds described in this paper.

When *p*-nitrobenzoyl chloride and the tin addition product were fused together dry, the interaction was so violent that there was a great deal of decomposition. This suggested the use of an indifferent solvent as diluent, to moderate the reaction, but the use of xylene in this way did not help matters much. However, when glacial acetic acid was used, a red reaction mixture was obtained, from which a very small quantity of the *p*-nitrophenyl thiazine was isolated. An acetic acid solution of fused sodium

[6] Heller and Nötzel, *J. prakt. Chem.*, [2] **76**, 59 (1907).

acetate was then tried, on the assumption that such a mixture, when used in an acylation reaction, would be more nearly comparable to the well-known Schotten–Baumann process and, as already recorded, this mixture was found to give excellent results when applied either to the tin chloride addition product or to the chlorostannate.

2-(*o*-Nitrophenyl)-*peri*-naphthothiazine (XV).—In the preparation of the di-(*o*-nitrobenzoyl)-aminomercaptan, it was noted that the mother liquor from the first precipitation of this crude diacyl derivative contained the corresponding thiazine.

When this mother liquor was diluted with water, a flocculent pale orange precipitate separated which, after decolorization and repeated crystallization from alcohol, gave flat orange needles of the thiazine, m. p. 166–168° (corr.); yield, 0.5 g. (from 11 g. of *o*-nitrobenzoyl chloride).

Anal. Calcd. for $C_{17}H_{10}O_2N_2S$: C, 66.63; H, 3.29. Found: C, 66.56; H, 3.24.

It was soluble in alcohol, acetic acid, ethyl acetate, benzene or chloroform. In concentrated hydrochloric acid or sulfuric acid, it dissolved to a red solution, from which it was reprecipitated on dilution.

Another run, carried out similarly, using the same quantity (10 g.) of chlorostannate, but only half as much of the *o*-nitrobenzoyl chloride (*i. e.*, 5.5 g. instead of 11 g.), yielded 0.6 g. (7%) of the pure thiazine and 2 g. of the mono-(*o*-nitrobenzoyl)-*peri*-aminonaphthyl mercaptan.

When 2 g. of the di-(*o*-nitrobenzoyl)-aminomercaptan was refluxed for an hour with a solution of 7.5 g. of fused sodium acetate in 100 cc. of glacial acetic acid, solution was complete after about twenty minutes' heating. As the solution cooled, gray needles were deposited which, when crystallized from xylene, proved to be the mono-(*o*-nitrobenzoyl)-aminomercaptan; yield, 0.5 g.

The filtrate from the crude mono-acyl derivative was poured into water. The flocculent orange precipitate, removed and purified by repeated crystallization from alcohol, was the thiazine (m. p. 166–168°, corr.); yield, 0.3 g.

The mono-(*o*-nitrobenzoyl)-aminomercaptan (1 g.), therefore, was refluxed for an hour with 2.5 g. of fused sodium acetate in 25 cc. of glacial acetic acid and, on cooling, 0.69 g. of unchanged initial material separated. The filtrate was poured into water and the flocculent orange solid which precipitated was purified by crystallization from alcohol and proved to be the thiazine, m. p. 165–167° (corr.); yield, 0.1 g.

2-(*m*-Nitrophenyl)-*peri*-Naphthothiazine (XI).—The chlorostannate (10 g.), glacial acetic acid (100 cc.) and fused sodium acetate (10 g.) mixture was shaken at about 60° with 5.5 g. of *m*-nitrobenzoyl chloride and the whole left overnight at room temperature. The orange precipitate was removed and the filtrate, on dilution with water, gave an additional amount of precipitate which was united with the first one. The total precipitate, decolorized and crystallized from glacial acetic acid, gave golden brown needles, m. p. 182.5–183° (corr.); yield, 4.9 g., or 55%.

Anal. Calcd. for $C_{17}H_{10}O_2N_2S$: C, 66.63; H, 3.29. Found: C, 66.78; H, 3.45.

The compound was soluble in alcohol, chloroform, ethyl acetate, glacial acetic acid or benzene. It dissolved in concentrated hydrochloric acid or sulfuric acid to a red solution and was reprecipitated therefrom by dilution.

The same product was obtained by refluxing for twenty minutes the di-(*m*-nitrobenzoyl)-aminomercaptan (0.7 g.) with 25 cc. of glacial acetic acid and 2.5 g. of fused sodium acetate. In five minutes a clear orange solution was obtained. As the solution cooled, the thiazine crystallized in golden brown needles, m. p. 182–183° (corr.); yield, 0.41 g., or 89%.

2-(*p*-Nitrophenyl)-*peri*-naphthothiazine (XI) was prepared in the same way as the *m*-isomer, except that the reaction was carried out at about 90° and the mixture was

allowed to stand for only four hours. The crude product, after decolorization and crystallization from glacial acetic acid, appeared in cherry red needles, m. p. 208.5–209° (corr.); yield, 5.2 g., or 58%.

Anal. Calcd. for $C_{17}H_{10}O_2N_2S$: C, 66.63; H, 3.29. Found: C, 66.61; H, 3.60.

It dissolved in alcohol, ethyl acetate, glacial acetic acid or benzene, and but sparingly in concentrated hydrochloric acid, from which latter solution dilution reprecipitated it.

This thiazine was also prepared from the di-(*p*-nitrobenzoyl)-aminomercaptan, by heating it in glacial acetic acid solution with fused sodium acetate, as described for the *m*-isomer. The m. p. of the product was 208.5–209° (corr.), and the yield 86%.

Further, it was found that when the di-(*p*-nitrobenzoyl)-aminomercaptan was heated alone for four to five minutes at 260–270°, *p*-nitrobenzoic acid sublimed, leaving behind the thiazine (m. p. 207–208.5°, corr.).

2-(*o*-Aminophenyl)-*peri*-naphthothiazine (XVI).—A mixture of 0.6 g. of the *o*-nitrophenylthiazine, 1.5 g. of stannous chloride, 5 cc. of concentrated hydrochloric acid and 50 cc. of alcohol, was refluxed for two hours. The solution was then made strongly alkaline with 5% sodium hydroxide solution, left for an hour at room temperature, the yellow precipitate collected, washed, dried and extracted with hot alcohol. The filtered alcohol extract was decolorized with norite, then diluted with hot water until turbid and allowed to cool. Golden yellow flat needles were obtained, which were further purified by a repetition of the treatment with alcohol and water, and then melted at 154–154.5° (corr.); yield, 0.37 g., or 68%.

Anal. Calcd. for $C_{17}H_{12}N_2S$: C, 73.87; H, 4.38; N, 10.14. Found: C, 73.69; H, 4.39; N, 10.31.

It was soluble in alcohol, ether, ethyl acetate, benzene or chloroform. Its red solution in concentrated hydrochloric or sulfuric acid was precipitated by dilution.

A more convenient method for the preparation of this compound was the direct reduction of the di-(*o*-nitrobenzoyl)-aminomercaptan (6.6 g.) with stannous chloride (22 g.), concentrated hydrochloric acid (40 cc.) and alcohol (400 cc.), carried out in the same way as above. The yield was 73% (2.7 g.), and the m. p. 154–154.5° (corr.). The advantage of this simultaneous reduction and cyclization was that it obviated the troublesome and rather difficult isolation of the pure *o*-nitrophenyl thiazine.

2-(*m*-Aminophenyl)-*peri*-naphthothiazine (XVI) was prepared from the nitrothiazine in much the same way as outlined in the first method given for the *o*-isomer, except that it was found advantageous to add some granulated tin also to the reducing mixture. Decolorized and crystallized from alcohol, the product formed silky yellow needles, m. p. 148–149° (corr.); yield, 3 g., or 59%.

Anal. Calcd. for $C_{17}H_{12}N_2S$: C, 73.87; H, 4.38; N, 10.14. Found: C, 73.91; H, 4.53; N, 10.10.

Its solubilities in alcohol, ethyl acetate, acetic acid, benzene and chloroform, were similar to those of the *o*-isomer. In concentrated hydrochloric acid or sulfuric acid it dissolved to red solutions from the latter of which it was partly reprecipitated by dilution, but not from the former.

2-(*p*-Aminophenyl)-*peri*-naphthothiazine (XVI) was obtained from the nitrothiazine as described in the first method given for the *o*-isomer, and crystallized from alcohol in golden yellow needles, m. p. 143–143.5°; yield, 3.45 g., or 76%.

Anal. Calcd. for $C_{17}H_{12}N_2S$: C, 73.87; H, 4.38; N, 10.14; S, 11.61. Found: C, 73.96; H, 4.73; N, 10.19; S, 11.41.

It dissolved in alcohol, ethyl acetate, acetic acid, benzene or chloroform. In concentrated hydrochloric acid it was but slightly soluble, and the resulting red solution was reprecipitated by dilution.

2-(*m*-Hydroxyphenyl)-*peri*-naphthothiazine (XIII).—After some experimentation, the following method of diazotization was found to give fair results.

After mixing 20 cc. of concentrated sulfuric acid with 15 cc. of water, 5 g. of the aminophenyl thiazine was dissolved in the still warm acid. The solution was cooled to 0°, 20 g. of cracked ice added and the diazotization effected by introducing beneath the surface, very slowly (twenty minutes), a solution of 1.2 g. of sodium nitrite in 6 cc. of water, keeping the temperature at 0–5° and adding sufficient cracked ice to bring the total volume up to about 100 cc. After standing for forty-five minutes longer at 0°, the gummy diazo product was decomposed by adding it slowly to boiling dilute sulfuric acid (75 cc. of concentrated acid + 75 cc. of water). When the mixture had cooled, it was diluted further. The black tarry product was removed, dried, dissolved in hot alcohol, the solution digested with norite, filtered hot and hot water added to the filtrate until it became turbid. As this turbid solution cooled, a crystalline product separated which was dissolved in dilute sodium hydroxide solution, filtered and the filtrate reprecipitated by carbon dioxide. Further purification by solution in hot alcohol, followed by dilution, gave clusters of orange needles, which began to sinter at 170° (corr.), but were not completely melted below 186° (corr.); yield, 1.5 g., or 30%.

Anal. Calcd. for $C_{17}H_{11}ONS$: C, 73.60; H, 4.0; N, 5.05. Found: C, 73.42; H, 4.28; N, 5.05.

The product dissolved in alcohol, ether, ethyl acetate, acetic acid, benzene, chloroform or sodium hydroxide solution. In either concentrated hydrochloric acid or sulfuric acid, it dissolved to a red solution reprecipitated by dilution.

2-(*p*-Hydroxyphenyl)-*peri*-naphthothiazine (XIII), prepared by the process outlined for the *m*-isomer, with a few minor modifications, was obtained in a yield of 34% for the crude product (m. p. 212–214°, corr.). By repeated crystallization from benzene, the m. p. was raised to 217–219° (corr.). In the course of this recrystallization, it was observed that the crystals separated by slow cooling of the solvent were orange, while those obtained by rapid cooling were paler and nearly yellow, but both had the same m. p. and the same streak.

Anal. Calcd. for $C_{17}H_{11}ONS$: C, 73.60; H, 4.0; N, 5.05. Found: C, 73.81; H, 4.11; N, 5.25.

The solubilities of this compound in alcohol, ether, ethyl acetate, acetic acid, benzene, chloroform and sodium hydroxide solution, were approximately the same as for the *m*-isomer. Concentrated hydrochloric acid imparted a red color to the crystals, but did not dissolve them.

Chloramine Yellow Dyes from the Aminophenyl-*peri*-naphthothiazines

1. From the *o*-Amino Derivative.—Sulfonation of the *o*-amino compound, either at 40–50° or at 90–100°, yielded a sulfo acid whose sodium and potassium salts were too difficultly soluble to warrant their attempted conversion into the dye.

2. From the *m*-Amino Derivative.—A solution of 2 g. of the amine in 50 cc. of concentrated sulfuric acid was heated for an hour at 40–50°, the solution poured upon cracked ice, the precipitate collected, dissolved in dilute ammonium hydroxide solution, filtered and the filtrate precipitated by acidification with concentrated hydrochloric acid. The dark brown product was dissolved in dilute sodium hydroxide solution and digested at room temperature for twenty-seven hours with a freshly prepared sodium hypochlorite solution. The dye was precipitated by adding a saturated salt solution. It was collected, redissolved in water, salted out again, removed and dried. It was soluble in water, but not in alcohol or in concentrated sodium hydroxide solution. In concentrated sulfuric acid it dissolved to a red solution. It dyed unmordanted cotton a tan, which was only moderately fast to light, laundering or bleeding. The dyeing was carried

out by heating for half an hour on a boiling water-bath the following mixture: 2.5 g. of unbleached cotton, 50 cc. of 0.1% dye solution (0.05 g. of dye), 62 cc. of water, 10 drops of 10% sodium carbonate solution and 37 cc. of 1% sodium chloride solution.

3. From the *p*-Amino Derivative.—This was prepared in the same way as the *m*-isomer. The dye was a purplish-red solid, soluble in water, but insoluble in alcohol or in concentrated sodium hydroxide solution. It dissolved slightly in concentrated sulfuric acid, to a reddish-brown solution. It dyed unmordanted cotton a burgundy shade, which was fast to light and also showed good fastness to laundering and to bleeding tests.

Summary

1. 2-R-*peri*-naphtho-*m*-thiazines have been synthesized from *peri*-aminonaphthyl mercaptans.

2. In methods of synthesis, structure and properties, these new products resemble closely the benzothiazoles.

3. A convenient process of acylation is described, in which complex tin derivatives of the amines are used as initial materials.

4. The new compounds described are the mono (*o*-nitrobenzoyl) and di (*o*-, *m*- and *p*-nitrobenzoyl) *peri*-aminonaphthyl mercaptans; the 2-methyl, 2-styryl, 2-(*o*-, *m*- and *p*-nitrophenyl), 2-(*o*-, *m*- and *p*-aminophenyl), 2-(*m*- and *p*-hydroxyphenyl) *peri*-naphthothiazines, and the phthalone of the 2-methyl compound.

5. The investigation is being continued.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TETRAPHENYL-DI-TERTIARY-BUTYLETHINYLETHANE

BY J. GAIL STAMPFLI AND C. S. MARVEL

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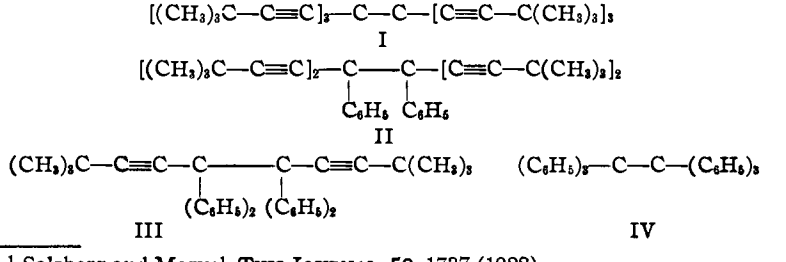
After the discovery that hexa-*tert.*-butylethinylethane (I) could be readily cleaved with sodium–potassium alloy and the liquid sodium amalgams,[1] an attempt was made to synthesize two other compounds, symmetrical diphenyl-tetra-*tert.*-butylethinylethane (II) and symmetrical tetraphenyl-di-*tert.*-butylethinylethane (III), in order to compare the stability of the ethane linkages in these three acetylenic hydrocarbons with that in hexaphenylethane (IV).



I

II

III IV

[1] Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928).