

optically active amide, and the Curtius rearrangement of an optically active acid azide. The fact that optically active products were not obtained in the experiments described by Jones and Wallis on *d*-benzylmethylacetylhydroxamic acid is shown to be due to secondary causes and not to racemization of the compound during rearrangement.

d-Benzylmethylacetylhydroxamic acid in the form of its benzoyl ester was allowed to rearrange in such a manner as to enable us to study the first product of the rearrangement, benzylmethylmethylisocyanate, and to observe its behavior toward polarized light. A benzene solution of this compound was dextrorotatory. *d*-Benzylmethylmethyl urea was prepared from this isocyanate and its specific rotation was found to be of the same value as the urea prepared from *d*-benzylmethylacetazide.

These facts point to the conclusion stated in part II of this series that in rearrangements of this type the radical, R, has either the same configuration as it had before rearrangement or that it undergoes complete inversion during its migration from the carbon atom to the nitrogen atom. Partial inversion seems unlikely.

PRINCETON, NEW JERSEY

RECEIVED NOVEMBER 12, 1932

PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Acenaphthene-*peri*-metathiazines and of Some Dyes Derived Therefrom¹

BY MARSTON TAYLOR BOGERT AND RICHARD B. CONKLIN

Introductory

Having completed in these laboratories the synthesis of the naphthalene-*peri*-metathiazines² (I), we turned our attention to the analogously constituted and hitherto unknown acenaphthene-*peri*-metathiazines (II), and this contribution records their successful synthesis from the 4-nitroacenaphthene-3-sulfonylchloride (IV). This synthesis supplies further corroboration of the constitution assigned to that nitrosulfo acid, as well as to those ascribed to the 3-nitro and 3-sulfo derivatives of acenaphthene.

The general plan of this synthesis involved the preparation of the 4-amino-3-acenaphthenylmercaptan (V) from the *peri*-nitrosulfonylchloride (IV) and, by treatment of this *peri*-aminomercaptan with acid chlorides, effecting ring closure and thiazine formation, as described by Reissert,³ and by Bogert and Bartlett,² in the naphthalene-*peri*-metathiazine group.

(1) The completion of this work was made possible by a generous grant from the Trustees of the Joseph Henry Fund of the National Academy of Sciences, to whom we wish to express our gratitude.—M. T. B. and R. B. C.

(2) Bogert and Bartlett, *THIS JOURNAL*, **53**, 4046 (1931).

(3) Reissert, *Ber.*, **55**, 858 (1922).

The flow sheet beyond exhibits diagrammatically the different steps carried out in this investigation.

The nitrosulfonchloride (IV) was reduced to the chlorostannate (VI), by the process developed by Bogert and Bartlett² in the naphthalene series, and this was used for the preparation of the desired acyl derivatives and thiazines, because it proved difficult and troublesome to obtain the aminomercaptan itself in satisfactory yield and purity. The acyl chlorides employed were benzoyl, *m*- and *p*-nitrobenzoyl.

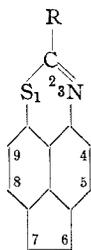
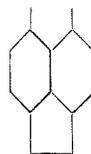
From the acylamino derivatives, the thiazines were obtained by digestion with a solution of fused sodium acetate in glacial acetic acid, a process of cyclization discovered by Bogert and Bartlett² in the naphthalene series. As in the latter series, so here this cyclization was accompanied with great increase in the depth of the color of the compounds and in their solubility in the solvents used.

The nitrophenylthiazines were readily reduced to the amines which, in turn, were sulfonated easily by concentrated sulfuric acid at 60–65°.

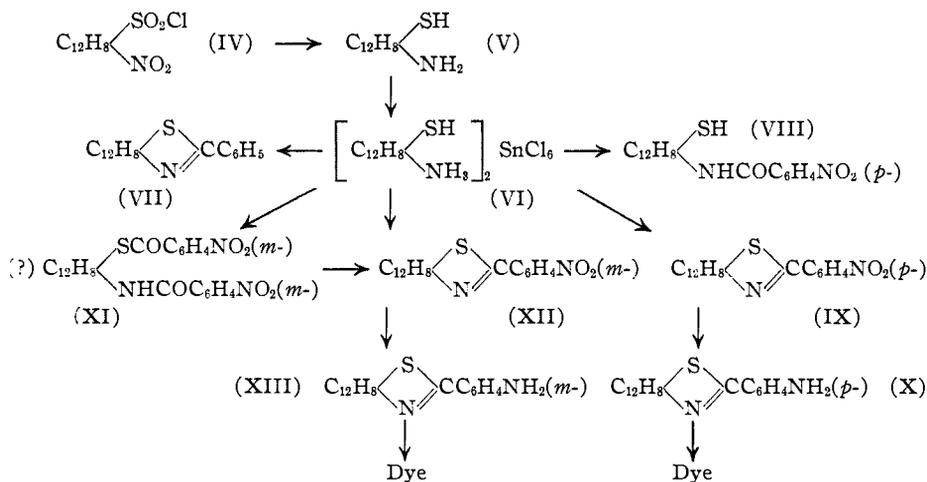
From the 2-(*m*-, and *p*-aminophenyl)-thiazines (X and XIII), dyes of Columbia Yellow (Chloramine Yellow) (Colour Index No. 814) type were prepared and their tinctorial properties compared with those of the similar dyes of the naphthalene series,² so as to learn what effect the presence of the ethylene bridge had upon these properties.

The dyeings on unmordanted unbleached cotton were not very different from the analogous naphthalene-*peri*-metathiazine dyes; that from the *m*-amino derivative gave a peach and from the *p*-isomer an apricot shade. In fastness to light and to bleeding, the dyes compared favorably with Columbia Yellow, but were less fast to laundering. Compared with the analogous naphthalene-*peri*-metathiazine dyes, they were equally fast to light and to laundering, and more stable to bleeding. They were not stable when left for some time in the presence of an excess of alkaline hypochlorite.

FLOW SHEET

(I) Naphthalene-*peri*-metathiazines(II) Acenaphthene-*peri*-metathiazines(III) C₁₂H₈

In the formulas below, the expression C₁₂H₈ is used to represent the complex (III) above.



Experimental

3-Amino-4-acenaphthenylmercaptan Chlorostannate (VI).—This was prepared by a variation of the process employed by Bogert and Bartlett² in the naphthalene series, as follows. A suspension of 59 g. of powdered hydrated stannous chloride in 180 cc. of glacial acetic acid was brought into solution by passing in a current of dry hydrogen chloride. The increase in weight was about 20 g. generally, but if continued above an increase of 24 g. the reaction mixture tended to froth over when the nitrosulfonchloride was introduced. To this solution there was added, all at once, 10 g. of finely pulverized nitrosulfonchloride (IV) and the mixture was shaken vigorously. Solution ensued quickly, the temperature rose rapidly to about 80°, and the chlorostannate separated in fine yellow needles. When the mixture had cooled, the precipitate was filtered out, washed thoroughly with glacial acetic acid, dry benzene and finally with dry ether; yield, 11.5 g., or 93%. The product was soluble in absolute alcohol, but practically insoluble in chloroform, ether, ethyl acetate or benzene. Water decomposed it immediately.

For analysis, an analytically pure sample of the nitrosulfonchloride was treated with the carefully filtered reducing solution. The product was washed as described above and dried in a desiccator over sulfuric acid and paraffin.

Anal. Calcd. for $(\text{HSC}_{12}\text{H}_8\text{NH}_3)_2\text{SnCl}_6$: C, 39.14; H, 3.29; SnO₂, 20.48; Cl, 28.91; S, 8.72. Found: C, 39.40; H, 3.19; SnO₂, 20.34; Cl, 28.96; S, 8.70.

The product dissolved in glacial acetic acid-sodium acetate mixtures with precipitation of sodium chloride. In glacial acetic acid solution it reacted with acid chlorides, forming acyl derivatives of the *peri*-aminomercaptan and *peri*-metathiazines.

Di(*m*-nitrobenzoyl) Derivative of 3-Amino-4-acenaphthenylmercaptan (XI).—The chlorostannate (5 g.) was decomposed by heating it at 90° with 5 g. of fused sodium acetate in 100 cc. of glacial acetic acid, and the resultant mixture was treated at 60° with 6 g. of *m*-nitrobenzoyl chloride added all at once; yield of crude product, 59%. Recrystallized from glacial acetic acid and decolorized, it formed long fine yellow needles, insoluble in concentrated hydrochloric acid or in sodium hydroxide solution. In concentrated sulfuric acid it dissolved to a yellow solution, from which it was reprecipitated by dilution. In hot alcohol it was practically insoluble, but dissolved in hot ethyl acetate or in acetone. When placed in a bath at 233° (corr.), it began to turn pink immediately and decomposed completely at about 235.5° (corr.).

Anal. Calcd. for C₂₆H₁₇O₆N₃S: C, 62.50; H, 3.43. Found: C, 62.67; H, 3.57.

When these experimental details were followed accurately, practically no thiazine (XII) was formed and there was no difficulty experienced in purifying the crude product as stated. Higher temperatures during the reaction gave appreciable amounts of the thiazine and variation of the other conditions likewise resulted in a product which could not be purified by crystallization from acetic acid.

3-*p*-Nitrobenzoylamino-4-acenaphthenylmercaptan (VIII).—Five grams of the chlorostannate was decomposed by heating it at 90° with a solution of 5 g. of fused sodium acetate in 50 cc. of glacial acetic acid. The resultant mixture was treated with 3.7 g. of powdered *p*-nitrobenzoyl chloride, added all at once, and the whole was shaken vigorously, refluxed for two hours and cooled. The precipitate was removed, washed with a little acetic acid and with water, and extracted with hot ethyl acetate (100 cc.) until the red color was removed. The insoluble portion (1.1 g.) was recrystallized from cellosolve and decolorized, when it formed pale brown microscopic needles which, when inserted in the bath at 245° (corr.), decomposed at 246–247° (corr.), turning dark red. The product was insoluble in sodium hydroxide solution or in concentrated hydrochloric acid. It dissolved in concentrated sulfuric acid to a yellow solution, from which it was reprecipitated by dilution with water. It was but slightly soluble in hot ethyl acetate, but in the presence of the thiazine dissolved sufficiently to render the isolation of the pure thiazine troublesome. In hot glacial acetic acid, it was but slightly soluble.

Anal. Calcd. for $C_{19}H_{14}O_2N_2S$: C, 65.11; H, 4.03; N, 7.82. Found: C, 65.51; H, 3.94; N, 8.07.

The thiazine also was formed in this reaction. Its preparation is described beyond.

2-Phenylacenaphthene-*peri*-metathiazine (VII).—To a solution of 5 g. of anhydrous sodium acetate in 50 cc. of glacial acetic acid at 90°, there was added 5 g. of the chlorostannate and the mixture was shaken at this temperature until all of the chlorostannate was decomposed (about ten minutes) and a clear orange solution resulted with precipitation of sodium chloride. Below 90°, this decomposition of the chlorostannate proceeded very slowly. A solution of 3 g. of benzoyl chloride in a few cc. of glacial acetic acid was then added all at once, the mixture was well shaken, allowed to stand for an hour, refluxed for an hour and a half and permitted to cool. The precipitate was removed, washed with a little acetic acid, then with water. There remained 0.5 g. of red needles, m. p. 105° (corr.). The red filtrate, poured into water, separated an orange precipitate which was collected and dried, and contained considerable tin. The combined precipitates were extracted with alcohol until the red color was completely removed. As the alcohol extract cooled, 1.1 g. of long feathery red crystals were deposited, m. p. 122–123° (corr.). By repeated crystallization and decolorizing in alcoholic solution, this changed to reddish-orange needles, which began to shrink and soften at about 128° and melted completely at 142.3° (corr.). The compound was easily soluble in alcohol, acetone, ethyl acetate or benzene.

Anal. Calcd. for $C_{19}H_{13}NS$: C, 79.39; H, 4.56; N, 4.88. Found: C, 79.45, 79.49; H, 5.25, 5.27; N, 5.22.

2-*m*-Nitrophenylacenaphthene-*peri*-metathiazine (XII).—When 5 g. of the di- (*m*-nitrobenzoyl) derivative (XI) was refluxed with a solution of 20 g. of fused sodium acetate in 200 cc. of glacial acetic acid, it dissolved within five minutes, forming a deep orange-red solution. The refluxing was continued for some forty minutes longer and the solution was then allowed to cool. The thiazine which separated was removed, washed with a little water, crystallized and decolorized in acetone solution; yield, 2 g. or 60%. It formed orange-red long glistening flat needles which, when placed in the bath at 183° (corr.), shrank at about 189° and melted with decomposition at 190.3–191.3° (corr.). The compound was freely soluble in ethyl acetate, glacial acetic acid or acetone, but only slightly in alcohol.

Anal. Calcd. for $C_{19}H_{12}O_2N_2S$: C, 68.63; H, 3.64; N, 8.44. Found: C, 68.72; H, 3.74; N, 8.59.

2-*p*-Nitrophenylacenaphthene-*peri*-metathiazine (IX).—This thiazine was formed during the production of the *p*-nitrobenzoyl mercaptan (VIII), but its isolation proved troublesome. It was found in the original acetic acid-sodium acetate solution, in the ethyl acetate extracts and the cellosolve mother liquors. Dilution of the original acetic acid-sodium acetate mother liquor with water gave a chocolate precipitate containing considerable tin. The ethyl acetate extracts, containing some precipitate, were cooled and yielded 1.1 g. of greenish solid, melting with decomposition at about 232°. The ethyl acetate filtrate from this was used to extract the chocolate precipitate from the acetic acid-sodium acetate solution, and in this way 0.25 g. more of crude thiazine was recovered. Finally, concentration of the cellosolve mother liquors gave about 0.3 g. of purer thiazine. These three lots of crude thiazine were combined and extracted repeatedly by refluxing with ethyl acetate. The thiazine thus isolated (1.1 g.) was purified by further crystallization and decolorizing in ethyl acetate, and then appeared in long lustrous needles, almost black in color, moderately soluble in hot glacial acetic acid, but only slightly soluble in hot alcohol. Its solutions were dark red. Placed in the bath at 244° (corr.), it decomposed at 253.7° (corr.).

Anal. Calcd. for $C_{19}H_{12}O_2N_2S$: C, 68.63; H, 3.64; N, 8.44. Found: C, 68.80; H, 3.55; N, 8.38.

It was prepared by decomposing 5 g. of the chlorostannate at 90° with 100 cc. of glacial acetic acid and 5 g. of fused sodium acetate, then treating this at 60° with 6 g. of *p*-nitrobenzoyl chloride, added in one lot. When the reaction was completed, the mixture was allowed to cool, the precipitate was removed, washed with acetic acid and with water, and then refluxed for three hours with 200 cc. of glacial acetic acid containing 20 g. of fused sodium acetate; yield, 2.25 g. of greenish black crystals of the thiazine, which melted with decomposition at about 243° (corr.), and were sufficiently pure for reduction to the corresponding amine (X).

2-*m*-Aminophenylacenaphthene-*peri*-metathiazine (XIII).—The corresponding nitro derivative (XII) (2 g.) was refluxed for two hours with a solution of hydrated stannous chloride (5.5 g.) in a mixture of alcohol (200 cc.) and concentrated hydrochloric acid (12 cc.). The deep red solution was poured into water, sodium hydroxide added to alkaline reaction, the mixture left for thirty minutes at room temperature, the precipitate removed, washed, dried, extracted with hot alcohol, the alcohol extracts decolorized and filtered. Water was added to the hot filtrate until incipient clouding, when it was permitted to cool. The separated amine (yield, 1.2 g., or 66%), recrystallized from alcohol and water in a similar manner, formed orange-yellow needles, soluble in methyl alcohol, acetone, ethyl acetate or benzene; slightly soluble in concentrated hydrochloric acid to a pale violet solution; but dissolving in concentrated sulfuric acid to a deep violet, changing gradually to a potassium permanganate color and then to shades of red, from which it was partially reprecipitated by the addition of water. When placed in the bath at 165° (corr.), it darkened and melted with decomposition at 176.7–177.7° (corr.).

Anal. Calcd. for $C_{19}H_{11}N_2S$: C, 75.45; H, 4.67. Found: C, 75.03; H, 4.78.

2-*p*-Aminophenylacenaphthene-*peri*-metathiazine (X) was prepared by reduction of the nitro derivative (IX) in much the same way as the *m*-isomer, except that some mossy tin was added to assist the reduction and three times the volume of alcohol was found necessary. The yield of crude amine was 72%, and the product formed orange needles which, when placed in the bath at 208° (corr.), gradually darkened and melted with decomposition at 214.8–215.8° (corr.). It was soluble in methyl alcohol, acetone, ethyl acetate or benzene. Its behavior with concentrated hydrochloric acid, or concentrated sulfuric acid, was the same as that of the *m*-isomer.

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.45; H, 4.67; S, 10.61. Found: C, 75.26; H, 4.36; S, 10.75.

Dyes of Columbia Yellow (Colour Index No. 814) Type from *m*- and *p*-Aminophenylacenaphthene-*peri*-metathiazines. From the *m*-Isomer.—When 1 g. of the amine was added to 30 cc. of concentrated sulfuric acid, it formed a solution of deep potassium permanganate color, which gradually changed to a deep wine red when the solution was heated for ten minutes at 60–65°. After cooling, the solution was poured upon ice, the flocculent orange precipitate collected, washed, dissolved in hot dilute sodium carbonate solution (leaving no insoluble residue), the hot solution acidified with hydrochloric acid, allowed to cool, the precipitate removed, washed and dried; yield, 1.3 g. of dark brown powder. This was dissolved in 250 cc. of hot very dilute sodium hydroxide, the solution cooled to room temperature, 3 cc. of 1.23 *N* sodium hypochlorite solution added and the mixture left for five hours at room temperature. It was then heated and an equal volume of hot filtered saturated salt solution added. The dye separated as a dark brown flocculent precipitate, which was filtered out when the solution was cold, dissolved in hot water, the solution filtered, the dye salted out again from the filtrate, washed with alcohol, ether and dried. It was insoluble in concentrated sodium hydroxide solution. In concentrated sulfuric acid, it dissolved with production of a port wine color. On prolonged contact with excess of alkaline hypochlorite, it was bleached to a pale yellow color, with marked increase in weight and loss of solubility in water.

The dyeings were carried out with 50 cc. of 0.1% dye solution, 2.5 g. of unbleached cotton, 62 cc. of water, ten drops of a 10% sodium carbonate solution and 37 cc. of a 1% sodium chloride solution, the mixture being heated for thirty minutes just below the boiling point.

Unmordanted unbleached cotton was thus dyed a peach shade, fast to light and bleeding, but only moderately fast to laundering.

From the *p*-Isomer.—The process was the same as for the *m*-isomer, varying only in some of the details.

The solution of the amine in the sulfuric acid, which was of potassium permanganate color at first, changed to a deep crimson red when heated. The crude aminosulfo acid was henna-colored when wet, but dark brown when dry; yield, 1.3 g. from 1 g. of the amine. The dye itself was a brown powder, slightly darker in color than its *m*-isomer, and in most of its physical, chemical and tinctorial properties resembled the latter, except that its dyeings on unbleached unmordanted cotton were of an apricot shade.

Summary

1. The synthesis of acenaphthene-*peri*-metathiazines has been accomplished, using 4-nitroacenaphthene-3-sulfonchloride as initial material, and their properties are described.

2. From the *m*- and *p*-aminophenylacenaphthene-*peri*-metathiazines dyes of Columbia Yellow (Colour Index No. 814) type have been prepared and their tinctorial properties recorded.

3. In preparation and properties, these metathiazines parallel closely the analogously constituted *peri*-metathiazines of the naphthalene series recently synthesized by Bogert and Bartlett.²

NEW YORK, N. Y.

RECEIVED NOVEMBER 14, 1932

PRINTED APRIL 6, 1933