Yellow crystals of the hydroquinone hydrochloride separated on cooling; yield, 0.2 g. (10%).

**Dibenzoyl isoquinoline-5,8-hydroquinone** formed colorless needles from alcohol, m. p. 162–163°.

*Anal.* Calcd. for $C_{23}H_{15}O_4N$: C, 74.78; H, 4.10. Found: C, 74.80; H, 4.28.

**Diacetyl 5(8)-amino-8(5)-hydroxyisoquinoline.**—This derivative was obtained from the dihydrochloride of the aminohydroxy compound with acetic anhydride and sodium acetate either in an aqueous solution (60% yield) or without a solvent (69% yield). It crystallizes from dilute alcohol as long, colorless needles, m. p. 208–209°.

*Anal.* Calcd. for $C_{13}H_{12}O_3N_2$: C, 63.91; H, 4.96. Found: C, 64.02; H, 5.13.

**5-Acetylamino-7-(*p*-sulfobenzeneazo)-8-hydroxyisoquinoline (or 8,6,5).**—The above diacetyl compound (2.41 g.) was dissolved in a cold solution of 1 g. of sodium hydroxide in 25 cc. of water (hydrolysis of the O-acetyl group) and the solution was treated at 0° with a suspension of the diazo compound from 2.09 g. of sulfanilic acid. A portion of the deep purple-red solution after being diluted yielded a brown, crystalline precipitate of the azo compound on acidification.

*Anal.* Calcd. for $C_{17}H_{14}O_5N_4S$: C, 52.82; H, 3.65. Found: C, 52.40; H, 3.99.

**5-Acetylamino-7-amino-8-hydroxyisoquinoline Dihydrochloride, VIII (or 8,6,5).**—The remainder of the solution of the azo compound was treated with sodium hydrosulfite and warmed gently until the color was discharged. The crystalline, yellow precipitate was dissolved in 20 cc. of water and 4 cc. of concentrated hydrochloric acid, and the clarified solution was saturated with hydrogen chloride at 0°, when fine yellow needles of the dihydrochloride soon separated; yield, 1.3 g. (43%). The salt is only moderately soluble in water but it is slow to crystallize.

*Anal.* Calcd. for $C_{11}H_{11}O_2N_3 \cdot 2HCl$: C, 45.52; H, 4.52. Found: C, 45.12; H, 4.70.

**5-Acetylaminoisoquinoline-7,8-quinone Hydrochloride, IX (or 8,6,5).**—A solution of 0.29 g. of VIII in 4 cc. of water and 0.5 cc. of concentrated hydrochloric acid was treated at 10° with 2 cc. of 20% ferric chloride solution added in one portion. The solution became red and fine, yellow needles soon separated. The product was washed free of dark mother liquor with concentrated acid, dissolved in 10 cc. of water, and 1 cc. of concentrated acid was added to the clarified solution. Golden yellow needles soon separated in 51% yield. Without isolating any of the intermediates, the yield from diacetyl aminohydroxyisoquinoline was 38%.

*Anal.* Calcd. for $C_{11}H_8O_3N_2 \cdot HCl$: Cl, 14.03. Found: 13.93, 13.94.

## Summary

Isoquinoline-5,8-hydroquinone has been prepared by three methods, and the oxido-reduction systems from this reductant and from the known quinoline-5,8-hydroquinone have been studied potentiometrically. An analysis is presented of the results obtained in this series of investigations of the degree of aromaticity of various heterocyclic rings.

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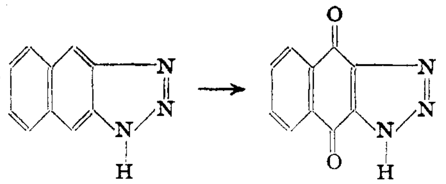
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# A Comparison of Heterocyclic Systems with Benzene. VII. Isologs of Anthraquinone Containing One and Two Triazole Rings

BY LOUIS F. FIESER AND ELMORE L. MARTIN

When this work was undertaken no unsubstituted quinones of the type indicated in the title were known, but in a paper published in March of this year Fries, Walter and Schilling(1) described the preparation of *lin*-naphthotriazole-8,9-quinone (II) by the oxidation of *lin*-naphthotriazole (I) with chromic anhydride. We had at the time performed a similar experiment, but the succession of steps leading to II was so generally unsatisfactory that a better method was developed.



I II

Ullmann and Ettisch(2) worked out an excellent method of preparing 2,3-dichloro-1,4-naphthoquinone from α-naphthol and found that one of the two chlorine atoms is easily replaced by reaction with ammonia. The halogen atom of the amino compound (III) is resistant to attack by amines under comparable conditions, but Fries and Ochwat(3) found that the acetyl derivative IV reacts normally with aromatic amines to give arylamino derivatives. On treating the acetyl compound IV with dry ammonia in nitrobenzene solution, we found that the substance is converted

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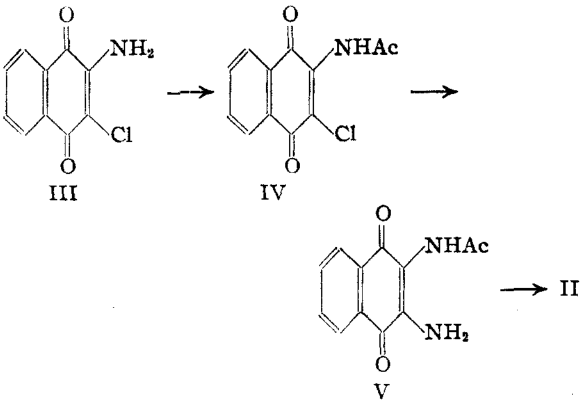
(1) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

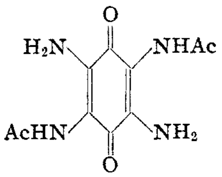
(2) Ullmann and Ettisch, *Ber.*, **54**, 270 (1921).

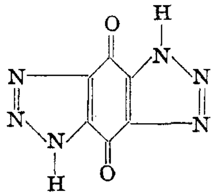
(3) Fries and Ochwat, *ibid.*, **56**, 1295 (1923).



smoothly into the amine V. We were at first unable to bring about a reaction of this substance with nitrous acid although the structure assigned was confirmed by the preparation of various derivatives. It was found that the difficulty is connected with the sparing solubility of the amine. When a solution of the colorless hydroquinone of V in dilute acid was treated with excess nitrous acid, a red precipitate of the quinone was produced in fine suspension, and in this condition it slowly reacted with the reagent with the formation of the desired *lin*-naphthotriazole-8,9-quinone, II, the acetyl group being hydrolyzed either during the reaction or in working up the product. On methylating the quinone II by the method described by Fries and co-workers,[1] we obtained a product identical with the 1-methyl-*lin*-naphthotriazole-8,9-quinone synthesized by Hartwell[4] by a method which establishes the structure.

Following the method described above, it was possible to prepare a *lin*-bis-triazoloquinone. Two of the halogen atoms of chloranil are easily replaced by amino groups, and it was found that after acetylation of these groups the remaining halogens can be caused to react with ammonia, giving VI. This substance is very sparingly soluble in most solvents and no reaction with nitrous acid could be brought about in an aqueous medium, even through the expedient found serviceable in the other series. The desired result was achieved by adding sodium nitrite to a suspension of VI in glacial acetic acid at 100°. The red diacetate gradually was transformed to a yellow, crystalline solid which proved to be the monosodium salt of 2,3,5,6-bis-triazolo-1,4-benzoquinone, VII. The quinone, which evidently is a very strongly acidic substance, was obtained by acidifying an aqueous solution of the salt with mineral acid. It decomposes explosively at a high temperature, and gives a characteristic anthraquinone vat test. The pure quinone is completely colorless, a remarkable property for substances of this class.[5]


VI


VII

Attempts to obtain the angular isomer of VII by the oxidation of 1,2,3,4-bis-triazolobenzene met with no success, but some improvements were made in the synthesis of the tricyclic compound and the details are recorded in the experimental part.

Unfortunately the two tricyclic quinones reported above do not dissolve to any appreciable extent in water, and a complete electrochemical characterization could not be made. In the case of *lin*-naphthotriazole-8,9-quinone it was possible to perform titrations of the reductant in alcoholic solutions, the potentials at half-oxidation against a hydrogen electrode in the same buffer at 25° being as follows: 0.4345 v. in 50% alcohol, 0.1 $N$ in hydrochloric acid and 0.2 $N$ in lithium chloride; 0.3450 v. in 37% alcohol, 0.047 $M$ in monopotassium phosphate and 0.047 $M$ in disodium phosphate. The difference between these two figures is in the direction which would be expected in a system whose oxidant has a strongly acidic group and whose reductant is basic.

## Discussion

Although the results are very meager, an interesting inference can be drawn from a comparison of the potential of *lir*-naphthotriazole-8,9-quinone in alcoholic hydrochloric acid (0.435 v.) with that of other tricyclic quinones in the same solvent. Since *lin*-naphthindazolequinone ($E_0$ = 0.155 v.) has practically the same potential as its 1-methyl ether VIII,[4] it would be safe to predict that the hydrogen compound corresponding to IX would have a potential close to that of IX. The fact that the value found for *lin*-naphthotriazole-8,9-quinone is so decidedly different, suggests that the structure may be represented more accurately by formula X.[6]

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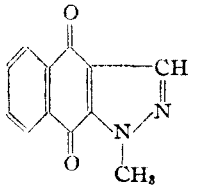
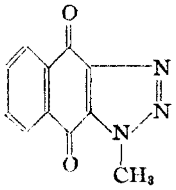
[4] Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).

[5] Compare *lin*-naphthindazolequinone, Fieser and Peters, *ibid.*, **53**, 4080 (1931).

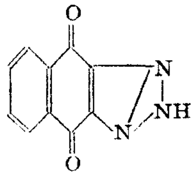
[6] Compare, Fieser and Ames, *ibid.*, **49**, 2604 (1927).



$E_0$ = 0.160 v.
VIII

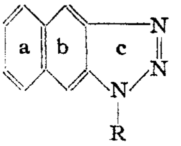


$E_0$ = 0.235 v.
IX

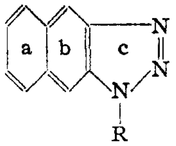


$E_0$ = 0.435 v.
X

As for the fine structure of the isologs of anthrahydroquinone or of anthracene containing a triazole nucleus, the electrochemical results favor the formulation XI, which indicates that Ring c, being less aromatic than Ring a, is the one which assumes the *o*-quinonoid or dihydride structure.

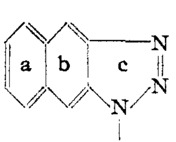


XI

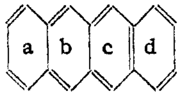


XII

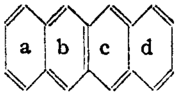
Fries,[1] on the basis of hydrogenation experiments, writes the alternate structure XII, in which Ring a is quinonoid, and the question is still open. We are in complete agreement with this author with regard to the principle involved, and indeed this was discussed previously by one of us with Ames.[6] At that time we failed to recognize a second principle set forth in the important paper by Fries, Walter and Schilling[1] to the effect that every ring of a polynuclear aromatic compound strives to approach as nearly as possible the condition of a true benzoid ring. According to this principle, to which we now subscribe, a structure such as XIII (or a similar structure for anthracene) is highly improbable, for two of the rings (b, c) have the dihydride structure.



XIII

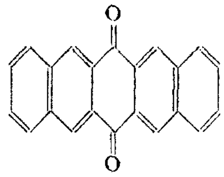


XIV

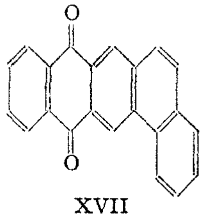


XV

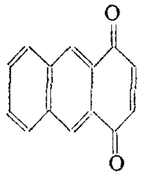
From a consideration of both of the influences determining the positions of the bonds, the formula for naphthacene XIV previously discussed[7] should be revised as in XV. In each formula two rings are quinonoid, but in XIV they are combined to form a highly unstable 2,3-naphthoquinonoid grouping (Rings a and b), while in XV two isolated and less reactive *o*-benzoquinonoid rings (a and d) are present. The fine structure previously written for naphthacenequinone[7] accords with the principle of greatest stability and it is similar to that assigned by Fries to pentacenequinone, XVI. Fries has expressed the view that, because of the special bond structure of the central nucleus, XVI is no *p*-quinone, and he considers that this explains the failure of the substance to form a vat. We do not share this view, but believe, rather, that the reluctance of XVI to undergo reduction is conditioned by a very low reduction potential. This is determined, not by the special structure of the quinone, but by the reactive quinonoid bond structure of the hydroquinone. This explanation has been advanced to account for a similar property of naphthacenequinone.[7] Clar's "2,3-phthaloylphenanthrene,"[8] which can be assigned the structure XVII, does not contain an ordinary *p*-quinone ring but it nevertheless gives the vat test (because the angular ring stabilizes the anthracene structure of the hydroquinone, giving a higher oxido-reduction potential).[9] Arguments have been advanced[10] for attributing to 1,4-anthraquinone the structure of XVIII, and the substance has all the properties of a true *p*-quinone in spite of the tetraketonic structure of the terminal ring.



XVI



XVII



XVIII

## Experimental Part

### 1. *lin*-Naphthotriazole-8,9-quinone

**2-Acetylamino-3-amino-1,4-naphthoquinone (V).**—Dry ammonia was passed into a boiling solution of 2.1 g. of pure 2-acetylamino-3-chloro-1,4-naphthoquinone[3] (m. p. 217–219°) in 15 cc. of nitrobenzene until there was no further color change and no further separation of ammonium chloride. The deep red solution on cooling deposited red crystals of the reaction product. The collected solid was washed with ether–ligroin, dried and washed with water to remove ammonium chloride; yield, 1.6 g. (83%); m. p. 225–230°. Crystallized from alcohol, in which it is only slightly soluble, the substance formed beautiful bright red needles, m. p. 233–234°. It dissolves

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(7) Fieser, This Journal, **53**, 2329 (1931).

(8) Clar, *Ber.*, **62**, 1574 (1929).

(9) Fieser and Dietz, This Journal, **53**, 1128 (1931).

(10) Fieser, *ibid.*, **50**, 465 (1928).

in alcoholic alkali with a deep red-purple coloration and is precipitated unchanged by acids; the solution in concentrated sulfuric acid has a light orange color.

*Anal.* Calcd. for $C_{12}H_{10}O_3N_2$: C, 62.58; H, 4.38; N, 12.2. Found: C, 62.19; H, 4.38; N, 11.9.

**2,3 - Di - (acetylamino) - 1,4 - naphthohydroquinone.**—An aqueous suspension of the quinone V was treated with sodium hydrosulfite and stirred until the red crystals disappeared and the colorless hydroquinone separated. This substance was dissolved in dilute hydrochloric acid, and one equivalent of acetic anhydride was added, followed by sodium acetate solution. The diacetyl derivative soon separated and it was recrystallized from dilute alcohol, forming colorless crystals, m. p. 255° dec., which turned yellow on storage.

*Anal.* Calcd. for $C_{14}H_{14}O_4N_2$: C, 61.29; H, 5.15. Found: C, 60.96; H, 5.19.

***lin*-Naphthotriazole-8,9-quinone** (II).—2-Acetylamino-3-amino-1,4-naphthoquinone (1.5 g.) was reduced as above and the nearly colorless product was collected and dissolved in 25 cc. of water and 3 cc. of concentrated hydrochloric acid. The slightly yellow solution was completely decolorized by filtration through a layer of Norite, and the filtrate, diluted to 50 cc., was treated at 0° with 10 cc. of 10% sodium nitrite solution. A fine, bright red precipitate separated immediately (collected at once, it was found to be the pure starting material), but on standing at 10–20° for two to three hours with the occasional addition of nitrite solution the color faded and finally a nearly colorless product resulted. This was collected, clarified in a dilute solution in alkali, and reprecipitated from the yellow filtrate. A solution of the faintly yellow material in hot acetone was decolorized with Norite, diluted with two volumes of warm water, and allowed to cool, when thin, glistening plates separated; yield 0.6 g. (46%). These crystals have a barely visible yellow tinge and they contain one molecule of water of crystallization which is lost on heating slightly above room temperature. The anhydrous compound decomposes at 240–245°. It does not dissolve in dilute acids. With alkaline hydrosulfite it forms a light red vat with an intensely green intermediate stage (quinhydrone).

*Anal.* Calcd. for $C_{10}H_5O_2N_3$: C, 60.28; H, 2.53. Found: C, 60.24; H, 2.82.

Fries, Walter and Schilling[1] state that their sample of this quinone was yellow and that the solution in dilute alkali was nearly colorless. Our quinone was nearly colorless and gave a faintly yellow solution in alkali. We obtained the same compound by the oxidation of *lin*-naphthotriazole in glacial acetic acid with chromic anhydride, but the yield was poor and the product was not obtained in a nearly colorless condition.

The N-methyl derivative, prepared by alkylation with dimethyl sulfate and alkali, formed colorless crystals from benzene, m. p. 248–250°. A mixture with Hartwell's sample[4] melted at 250–251°.

### 2. *lin*-bis-Triazoloquinone

**2,5-Diamino-3,6-dichloroquinone.**—The method of von Knapp and Schultz[11] was improved considerably by passing dry ammonia into a suspension of 12.3 g. of finely powdered chloranil in 150 cc. of boiling alcohol until the yellow crystals had dissolved. Dark red crystals of the diamine separated along with the ammonium chloride. After cooling, the solid was washed with water, alcohol, and ether, leaving 7.8 g. (75%) of deep red needles. Finding no suitable recrystallizing solvent, the material was purified as follows. A suspension of 1 g. of the quinone in aqueous hydrosulfite solution was warmed slightly to effect reduction. The nearly colorless hydroquinone was dissolved in dilute hydrochloric acid and the solution was decolorized by filtration through a layer of Norite, diluted to 200 cc., and treated at 90° with excess ferric chloride solution. The quinone separated slowly as long fine, deep red needles (0.8 g.).

**2,5-Di-(acetylamino)-3,6-dichloroquinone.**—A suspension of 8.2 g. of the diaminoquinone in 25 cc. of acetic anhydride was treated with ten drops of concentrated sulfuric acid and stirred at room temperature until conversion to bright yellow crystals of the diacetyl compound was complete. Alcohol was added to the cooled mixture and the product was collected; yield, 8.7 g. (75%); m. p. 240–245°. The substance is moderately soluble in glacial acetic acid and slightly soluble in alcohol. It crystallizes well from either solvent as yellow needles, m. p. 253–254°.

*Anal.* Calcd. for $C_{10}H_8O_4N_2Cl_2$: C, 41.24; H, 2.77. Found: C, 41.36; H, 2.95.

**2,5-Di-(acetylamino)-3,6-diaminoquinone** (VI).—The reaction of the diacetylaminodichloroquinone with ammonia did not proceed well in boiling nitrobenzene solution, the material being largely destroyed. A better method consisted in passing dry ammonia into a suspension of 8.2 g. of the finely powdered material in 100 cc. of boiling alcohol and allowing most of the alcohol to evaporate as the reaction progressed. A reddish-brown product separated, and after cooling this was collected and washed with water, alcohol and ether, giving 5.6 g. (79%) of material suitable for the next step. The quinone is sparingly soluble in most solvents and no recrystallizing solvent was found. A purification was accomplished by dissolving the brown-red material (0.25 g.) in a mixture of 25 cc. each of alcohol and water containing 1 cc. of 10% alkali, filtering the purple-red solution, and acidifying. Fine, dark red needles separated slowly. The substance has no characteristic point of decomposition; the solution in concentrated sulfuric acid is deep red and becomes yellow on the addition of a small amount of water. Carbon–hydrogen analyses were unsatisfactory.

**2,3,5,6-Bistriazolo-1,4-benzoquinone** (VII).—A suspension of 0.5 g. of the crude quinone VI in 20 cc. of glacial acetic acid was warmed on the steam-bath and treated with 20 cc. of 10% sodium nitrite solution, added slowly in portions. The dark starting material slowly dissolved and the color of the solution faded to a light red. Solid sodium nitrite was added until the color changed to a light yellow and yellow crystals of the sodium salt of the reaction product separated. After cooling, the crystals were washed with cold water, alcohol and ether. The substance crystallized from water as stout, bright yellow needles of the **monosodium salt dihydrate**; yield, 0.2 g.

*Anal.* Calcd. for $C_6HN_6O_2Na \cdot 2H_2O$: N, 33.9. Found: N, 34.0.

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(11) Von Knapp and Schultz, *Ann.*, **210**, 183 (1881).

The quinone itself separated as completely colorless microcrystals on acidifying a hot, clarified, aqueous solution of the sodium salt; yield, 0.15 g. (40%). The substance is insoluble in the usual solvents and it could not be recrystallized, but the above material appeared to be pure.

*Anal.* Calcd. for $C_6H_2O_2N_4$: C, 37.89; H, 1.06. Found: C, 38.12; H, 1.20.

The colorless quinone gives a yellow vat with alkaline hydrosulfite solution, and on shaking with air the solution acquires a beautiful blue color, probably as the result of quinhydrone formation. In the presence of excess reducing agent the color fades to yellow on standing, and the test can be repeated until the reagent is exhausted, when the sparingly soluble sodium salt of the quinone separates. The quinone is unaffected at temperatures up to 300°; when heated on a spatula it decomposes with explosive violence.

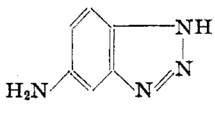
### 3. Preparation of *lin*-Naphthotriazole (I)

As the procedure of Friedländer and v. Zakrzewski[12] for preparing **potassium 2,3-dihydroxynaphthalene-6-sulfonate** gave very poor results, the following method was developed. Technical 2-naphthol-3,6-disulfonic acid (120 g.) was added rapidly with stirring to a melt at 200° from 460 g. of potassium hydroxide, 20 g. of sodium hydroxide, and 6 cc. of water. In the course of twenty minutes the temperature was raised to 250°, when the yellow melt changed to an even paste. The melt while hot was transferred in portions to 1 kg. of ice and 730 cc. of concentrated hydrochloric acid, and the red-brown solution was treated with active charcoal, filtered and acidified. The slightly colored salt which separated on cooling was dissolved in hot water saturated with sulfur dioxide and after clarifying the solution with active charcoal, the colorless filtrate deposited 50 g. (52%) of glistening, colorless plates. The addition of ferric chloride to the aqueous solution produces a beautiful intense blue-violet coloration.

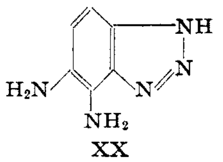
**2,3-Dihydroxynaphthalene**[12] was obtained by heating 30 g. of the above sulfonate with 240 cc. of water and 45 cc. of concentrated sulfuric acid for twelve hours in an autoclave at 150–160°; yield, 13 g. (65%); m. p. 158–159°. This was converted into 2,3-diaminonaphthalene by the method of Morgan and Godden.[13] The conversion was nearly quantitative in successful experiments, but few tubes withstood the drastic conditions. The method of the above authors was used for closing the triazole ring.

### 4. Preparation of 1,2,3,4-bis-Triazolobenzene

This compound (XXI) has been obtained[14] from 5-aminobenzotriazole (XIX) through the diamino compound XX.



XIX



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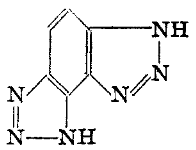
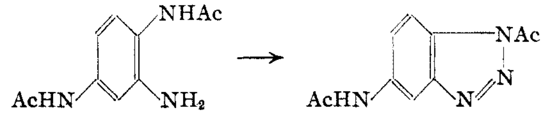


XXI

An improved method of preparing XIX was found in nitrating diacetyl *p*-phenylenediamine, reducing the nitro compound catalytically, converting the amine XXII with nitrous acid into the diacetyl compound XXIII and hydrolyzing the latter compound.



XXII XXIII

**2,5-Di-(acetylamino)-aniline (XXII).**—2,5-Di-(acetylamino)-nitrobenzene, m. p. 186–188°, was obtained in 83% yield by Ladenburg's method,[15] and 19.7 g. of this material dissolved in 300 cc. of hot alcohol was hydrogenated in the presence of 0.1 g. of Adams catalyst. The amino compound (XXII) was collected and a solution of the material in dilute acid was clarified with Norite. On neutralization the substance separated in a colorless condition; yield, 15 g. (87%); m. p. 235–237° (recrystallized from alcohol, m. p. 236–237°).[16]

**5-Aminobenzotriazole Dihydrochloride.**—The slow addition of 70 cc. of 10% sodium nitrite solution to a cold solution of 20.7 g. of XXII in 150 cc. of water and 17.7 cc. of concentrated hydrochloric acid gave 20.6 g. (95%) of 5-aminobenzotriazole diacetate, m. p. 182–184° (recrystallized from acetone–water, m. p. 184–185°, literature,[17] 184°). For the hydrolysis, 4.36 g. of the diacetate was boiled with 10 cc. of concentrated hydrochloric acid for one hour, adding a trace of stannous chloride to discharge a faint yellow color. On cooling at 0°, stout colorless needles of the dihydrochloride separated; yield, 4 g. (90%).

**4,5-Diaminobenzotriazole (XX)** was prepared from XIX through the benzeneazo compound. The latter substance was obtained by coupling in the presence of sodium acetate according to Fries, Güterbock and Kühn,[17] but it was more conveniently collected as the hydrochloride. This was obtained as a mass of fine, bright red needles by adding dilute acid to the orange, gelatinous precipitate of the azo compound, yield 95%. The substance dissolves in dilute alkali and an excess of reagent precipitates the orange sodium salt. For the reduction, 5.49 g. of the hydrochloride was stirred at room temperature with a solution of 9 g. of stannous chloride crystals in 50 cc. of concentrated hydrochloric acid. After gentle warming the resultant yellow mixture was cooled and the precipitated material was recrystallized twice from hydrochloric acid solution; fine yellow needles, 3.2 g. (69%).

**1,2,3,4-bis-Triazolobenzene (XXI).**—On treating XX with nitrous acid according to Nietzki and Prinz,[14] most of the material was destroyed by oxidation. This was

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[12] Friedländer and v. Zakrzewski, *Ber.*, **27**, 761 (1894).

[13] Morgan and Godden, *J. Chem. Soc.*, **97**, 1718 (1910).

[14] Nietzki and Prinz, *Ber.*, **26**, 2960 (1893).

[15] Ladenburg, *ibid.*, **17**, 148 (1884).

[16] Bülow and Mann, *ibid.*, **30**, 986 (1897), prepared the compound by reduction with iron and acetic acid and reported a melting point of 231–232°.

[17] Fries, Güterbock and Kühn, *Ann.*, **511**, 221 (1934).

prevented to some extent by protecting one of the amino groups by acetylation.

A solution of 1.16 g. of 4,5-diaminobenzotriazole dihydrochloride and 0.6 cc. of acetic anhydride in 100 cc. of water was treated quickly with a solution of 1 g. of fused sodium acetate in water. The light yellow solution was clarified with charcoal, cooled to 0°, and treated slowly with 4 cc. of 10% sodium nitrite solution. The nearly colorless precipitate (acetate) was dissolved in warm 2% sodium hydroxide solution and precipitated with dilute acid, giving 0.2 g. (25%) of the almost colorless bis-triazolobenzene.

## Summary

Methods have been developed for the synthesis of isologs of anthraquinone with either one or two of the benzene rings replaced by a triazole ring. Unfortunately these compounds proved to be so sparingly soluble that only a very limited potentiometric characterization was possible, but the results obtained have some bearing on the problem of the fine structure of the triazole nucleus. This paper includes also a comparison with the views of Fries concerning the bond structure of polynuclear hydrocarbons and quinones.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, TEACHERS COLLEGE, COLUMBIA UNIVERSITY]

# Studies of Crystalline Vitamin $B_1$.[1] X. Sulfite Cleavage. III. Chemistry of the Basic Product

BY EDWIN R. BUCHMAN, ROBERT R. WILLIAMS AND JOHN C. KERESZTESY

By cleavage of vitamin $B_1$ with sulfite Williams[2] obtained a basic substance $C_6H_9NSO$ (II), easily isolated as the crystalline hydrochloride in yields up to 97%. The free base is a colorless, rather viscous oil with a characteristic faint basic odor, easily soluble in water, alcohol and chloroform and less readily in ether. It is a mono acid base giving well-defined crystalline derivatives with chloroplatinic, picric and picrolonic acids.

The evidence[3] points to the presence of a free hydroxyl group in the vitamin. Since the oxygen in (II) is evidently derived directly from the vitamin, attempts were made to demonstrate an hydroxyl in (II). With concentrated hydrochloric acid at 150° it was found, as expected, that —OH is replaced by non-ionic chlorine

$$C_6H_9NSO\ (II) \xrightarrow{HCl} C_6H_8NSCl\ (V)$$

(V), obtained in good yield in the form of its crystalline hydrochloride, closely resembles the oxy base (II); the ultraviolet absorption spectra are nearly identical.[4]

When treated with excess *p*-nitrobenzoyl chloride in pyridine, (II) gave a crystalline mononitrobenzoate which still exhibited basic properties. Evidently only the —OH group reacts with acyl chlorides and it may be assumed that the nitrogen in (II) is tertiary in character.

The action on (II) of nitrous acid and of methyl iodide was studied to secure further evidence on this point. With nitrous acid a crystalline product was obtained in good yield, but its analysis and properties showed it to be the nitrate of the original base, $C_6H_9NSO{\cdot}HNO_3$. With methyl iodide a typical quaternary salt was obtained by allowing the two components to combine slowly at room temperature.

$$C_6H_9NSO\ (II) \xrightarrow{CH_3I} C_6H_9NSO{\cdot}CH_3I\ (VI)$$

Treatment of the salt (VI) with alkali regenerated no ether-soluble base. In striking contrast to (II) which after heating with 20% alkali at 100° can be recovered unchanged, (VI) under the same conditions was completely destroyed with formation of alkali sulfide. The vitamin itself is readily attacked by hot alkali, also splitting out sulfide.[5] This analogy is consistent with the view that the vitamin is a quaternary salt of (II).[6]

While this investigation was in progress there appeared an article[7] by Windaus, Tschesche and Grewe describing the splitting of the vitamin with nitric acid and the isolation of two well-characterized degradation products, one a sulfur-containing acid $C_5H_5NSO_2$. Oxidation of (II) with nitric acid at 40° gave sulfuric acid and 30% of an acid (VII).

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(1) Presented before the Organic Division of the American Chemical Society at the New York Meeting, April, 1935.

(2) R. R. Williams, R. E. Waterman, J. C. Keresztesy and E. R. Buchman, THIS JOURNAL, **57**, 536 (1935).

(3) E. R. Buchman and R. R. Williams, *ibid.*, **57**, 1751 (1935).

(4) A. E. Ruehle, *ibid.*, **57**, 1887 (1935).

(5) A. Windaus, R. Tschesche, H. Ruhkopf, F. Laquer and F. Schultz, *Nachr. Ges. Wiss. Göttingen. Math.-phys. Klasse*, III, 211 (1931).

(6) R. R. Williams, THIS JOURNAL, **57**, 229 (1935).

(7) A. Windaus, R. Tschesche and R. Grewe, *Z. physiol. Chem.*, **228**, 27 (1934).