An analytical sample prepared by crystallization from benzene melted at 215–217°.

Anal. Calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.00; H, 5.34; N, 11.64.

4,4'-Bicinnolyl sulfide. A solution of 2.0 g. of 4-chlorocinnoline, 2.0 g. of 4-mercaptocinnoline and 0.67 g. of sodium methoxide in 35 ml. of dry methanol was refluxed for 1.75 hr. The product, 3.5 g. (97%), separated from the hot solution, m.p. 180–181°. A sample purified for analysis by crystallization from ethanol melted at 181°.

Anal. Calcd. for $C_{16}H_{10}N_4S$: C, 66.21; H, 3.47; N, 19.31. Found: C, 66.07; H, 3.51; N, 18.90.

4,4'-Bis(6,7-dimethoxycinnolyl) sulfide. A solution of 1.4 g. of 4-chloro-6,7-dimethoxycinnoline, 1.4 g. of 6,7-dimethoxy-4-mercaptocinnoline, and 0.34 g. of sodium methoxide in 23 ml. of dry methanol was refluxed for 2.5 hr., whereupon the solid product separated from the hot solution. There was obtained 2.4 g. of crude product, m.p. 210–215°. An analytical sample was prepared by crystallization from a large volume of ethanol, m.p. 220–225°.

Anal. Calcd. for $C_{20}H_{18}N_4SO_4$: C, 58.52; H, 4.42; N, 13.65. Found: C, 58.70; H, 4.62; N, 13.34.

4-Cinnolyl 4'-(6',7'-dimethoxycinnolyl) sulfide. A solution of 2.8 g. of 4-chloro-6,7-dimethoxycinnoline, 2.0 g. of 4-mercaptocinnoline, and 0.67 g. of sodium methoxide in 45 ml. of dry methanol was refluxed for 3.5 hr., at which time a solid product separated amounting to 4.24 g., m.p. 193°. The analytical sample was crystallized from ethanol, m.p. 193°.

Anal. Calcd. for $C_{18}H_{14}N_4O_2S$: C, 61.70; H, 4.03; N, 15.99. Found: C, 61.62; H, 4.29; N, 15.70.

4-Cinnolyl 2-quinoxalyl sulfide. A solution of 1.5 g. of 2-chloroquinoxaline, 1.5 g. of 4-mercaptocinnoline and 0.5 g. of sodium methoxide in 26 ml. of dry methanol was refluxed for 8.5 hr. Only 0.25 g. of product was obtained, which after purification by crystallization from ethanol melted at 153–154°, pale yellow needles.

Anal. Calcd. for $C_{16}H_{10}N_4S$: C, 66.21; H, 3.47; N, 19.31. Found: C, 66.02; H, 3.69; N, 18.97.

4-(6,7-Dimethoxycinnolyl) 2-quinoxalyl sulfide. A solution of 1.5 g. of 2-chloroquinoxaline, 2.1 g. of 6,7-dimethoxy-4-mercaptocinnoline, and 0.5 g. of sodium methoxide in 26 ml. of dry methanol was refluxed for 2.25 hr. The solid product amounted to 1.85 g., m.p. 210°. A sample purified for analysis by crystallization from ethanol melted at 210°.

Anal. Calcd. for $C_{18}H_{14}N_4O_2S$: C, 61.70; H, 4.03; N, 15.99. Found: C, 61.33; H, 4.18; N, 16.30.

4,6,7-Trimethoxycinnoline. A solution of 1.0 g. of 4-chloro-6,7-dimethoxycinnoline and 0.5 g. of sodium methoxide in 30 ml. of absolute methanol was refluxed for 2.5 hr. The solution was allowed to cool and stand overnight whereupon 0.74 g. (76%) of product separated, m.p. 210° dec. An analytical sample was prepared by crystallization from methanol, m.p. 210° dec.

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49. Found: C, 59.74; H, 5.76.

4-Ethoxy-6,7-dimethoxycinnoline. A solution of 1.0 g. of 4-chloro-6,7-dimethoxycinnoline and 0.5 g. of sodium ethoxide in 30 ml. of absolute ethanol was refluxed for 2 hr. Some solid product separated during the heating period and additional material separated on standing overnight at room temperature. Upon purification of the nonhomogeneous solid by repeated crystallization from ethanol, 0.15 g. of 4-chloro-6,7-dimethoxycinnoline was recovered together with 0.3 g. of product, m.p. 185–187°.

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.95. Found: C, 61.67; H, 6.17; N, 11.90.

Infrared spectra were determined on all compounds except 4-ethoxy-6,7-dimethoxycinnoline and 4-cinnolyl-4'-(6',7'-dimethoxycinnolyl) sulfide. All these compounds show the characteristic cinnoline absorption band[1] in the 6.3 μ region, although the absorption is weak in some instances. These spectra were determined as Nujol mulls on the Perkin-Elmer Infracord.

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[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID COMPANY]

Some Carboxaldazines and *s*-Triazoles of the Anthraquinone Series

ERWIN KLINGSBERG

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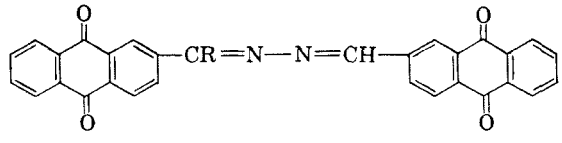
2-Anthraquinonecarboxaldazine (I) reacts with chlorine to give the α-monochloro derivative (II) or 2-cyanoanthraquinone (VI), depending on conditions. 1,1'-Dichloro-2-anthraquinonecarboxaldazine (XI) behaves similarly. II reacts with amines to give aminoaldazines or triazoles.

The present paper describes the results of an investigation into the preparation and reactions of certain chlorinated anthraquinonecarboxaldazines, undertaken with a view to the synthesis of anthraquinonyltriazoles.[1]

Stollé,[2,3] found that benzaldazine takes up one or two atoms of chlorine, according to conditions, to give the monochloro derivative $C_6H_5CCl{:}N{-}N{:}CHC_6H_5$ or the dichloro derivative $C_6H_5CCl{:}N{-}N{:}CClC_6H_5$. The behavior of 2-anthraquinonecarboxaldazine (I) is somewhat different. While it

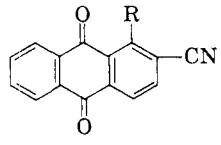


	R =
I	H
II	Cl
III	NH_2
IV	NHMe
V	NMe_2

does react with chlorine in nitrobenzene at 100–140° to give the monochloro derivative (II), a second atom of chlorine could not be introduced. When the reaction temperature was raised to 160–165°, a poor yield of unidentified product was obtained.

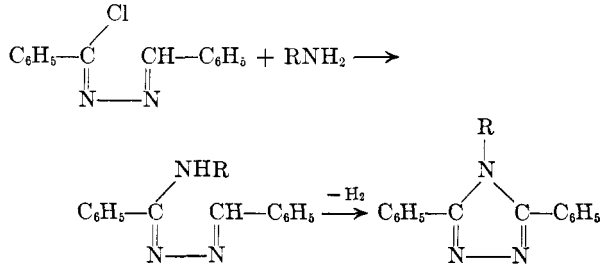
(1) E. Klingsberg, *J. Am. Chem. Soc.* **80**, 5786 (1958).
(2) R. Stollé, *J. Prakt. Chem.* **85**, 386 (1912).
(3) R. Stollé and Fr. Helwerth, *Ber.*, **47**, 1132 (1914).

Chlorination in *o*-dichlorobenzene at this temperature gave a good yield of 2-cyanoanthraquinone (VI); this cleavage reaction, giving benzonitrile from benzaldazine, was also observed by Stollé.[2]



R =
VI H
VII Cl

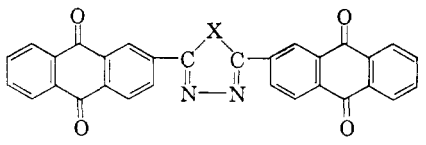
Monochlorobenzaldazine reacts with ammonia and primary amines to give *s*-triazoles by spontaneous air-dehydrogenation of the initial reaction product[3]:



R = H, alkyl, phenyl

Again, the anthraquinone derivatives behaved somewhat differently. The reaction product with ammonia had the open-chain structure (III), as shown by infrared absorption in the NH stretching region at 2.95 and 3.04 μ, characteristic of primary amines. Thus, dehydrogenation did not occur even though aminolysis was conducted in nitrobenzene at 180–190°. The structure of the product was confirmed by nitrosylsulfuric acid degradation under mild conditions to 2-anthraquinonecarboxaldehyde; this behavior would be expected of III but not of a triazole.

Similarly the methylamine reaction product, an orange solid, m.p. 329–330°, had the open-chain structure (IV), as shown by a single infrared absorption band in the NH stretching region at 2.94 μ and absorption at 6.60 μ in the NH deformation region. Confirmation of structure was afforded by treatment with potassium hydroxide in diethylene glycol monoethyl ether at 155°. The product was a pale yellow neutral solid, m.p. 358–360°. Analysis showed that it contained two less hydrogen atoms than the starting material, and as it showed no absorption at 2.94 μ and much weaker absorption at 6.60 μ, this was clearly the triazole (VIII). Under these conditions III was not cyclized, but



X =
VIII NCH_3
IX NC_6H_5
X O

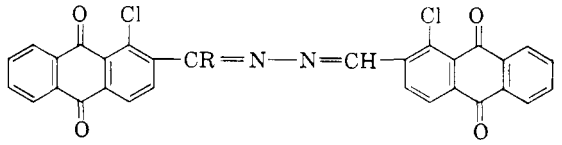
was recovered unchanged.

The reaction product of II with aniline was also lacking in absorption near 2.9 and 6.5 μ, and was thus the triazole IX, formed by spontaneous cyclodehydrogenation during aminolysis. It was recovered unchanged after treatment with potassium hydroxide in diethylene glycol monoethyl ether at 155°.

The dimethylamine reaction product is, of course, incapable of cyclodehydrogenation and must be V.

The oxadiazole (X) was prepared by cyclodehydration of 1,2-bis(2-anthraquinonecarbonyl)hydrazine in oleum or polyphosphoric acid.

Attention was then turned to the 1-chloro derivatives of this series of compounds. 1-Chloro-2-anthraquinonecarboxaldehyde was prepared by the excellent procedure of Hershberg and Fieser[4] and converted to the aldazine (XI). In its behavior on



R =
XI H
XII Cl

chlorination, it resembles I. At 95° in nitrobenzene it took up a single atom of chlorine to give XII. The occurrence of chlorination in the side-chain rather than the nucleus was proved by sulfuric acid degradation to 1-chloro-2-anthraquinonecarboxylic acid and 1-chloro-2-anthraquinonecarboxaldehyde; the latter was not isolated as such but was converted to the aldazine (XI) under the conditions of the degradation. Chlorination of XI in *o*-dichlorobenzene at higher temperatures caused cleavage to 1-chloro-2-cyanoanthraquinone (VII).

Aminolysis of the side-chain chlorine atom in XII was not successful with ammonia, aniline, or other amines. Relatively mild reaction conditions gave unchanged starting material, while more severe conditions caused decomposition. Apparently the nuclear and side-chain atoms are too similar in reactivity to permit selective displacement.

EXPERIMENTAL[5]

2-Anthraquinonecarbonyl chloride 2-anthraquinonylmethylenehydrazone (II). A mixture of 0.50 g. (1.07 mmoles) of 2-anthraquinonecarboxaldazine (I) and 20 ml. of nitrobenzene was heated in an oil bath at 125–135° and subjected for 3 hr. to a vigorous stream of chlorine. The internal temperature of the mixture was 110–115°. The product was then cooled, filtered, and washed with a little benzene. Yield, 0.50 g. (93%) of bright yellow solid, m.p. 321–325° dec. On crystallization from chlorobenzene, the m.p. fell to 316–319° dec.

Anal. Calcd. for $C_{30}H_{15}ClN_2O_4$: C, 71.6; H, 3.0; Cl, 7.1; N, 5.6. Found: C, 71.7; H, 3.2; Cl, 7.4; N, 5.8.

2-Cyanoanthraquinone (VI). A mixture of 0.20 g. (0.43 mmole) of 2-anthraquinonecarboxaldazine (I) and 3 ml. of

(4) E. B. Hershberg and L. F. Fieser, *J. Am. Chem. Soc.*, **63**, 2561 (1941).

(5) Melting points are corrected.

o-dichlorobenzene was heated in an oil bath at 160–165° and treated with a stream of chlorine for 2 hr. The mixture, at first thick, slowly dissolved to an almost colorless solution. The yellow product that separated on cooling was filtered and washed with benzene. Yield, 0.20 g., m.p. 216–217°. It was purified by crystallization from acetic acid, without change in melting point.

Anal. Calcd. for $C_{15}H_7NO_2$: C, 77.3; H, 3.0; N, 6.0; O, 13.7. Found: C, 77.3; H, 3.3; N, 6.0; O, 13.6.

2-Anthraquinonecarboxamide 2-anthraquinonylmethylenehydrazone (III). A steady stream of ammonia was passed for 5 hr. through a suspension of 0.55 g. (1.10 mmoles) of II in 10 ml. of nitrobenzene in an oil bath at 210–220°; the internal temperature was 175–180°. The mixture was then cooled, diluted with a little alcohol, and filtered, giving 0.49 g. (91%) of orange product unmelted at 365°. It was purified by crystallization from dimethylformamide.

Anal. Calcd. for $C_{30}H_{17}N_3O_4$: C, 74.5; H, 3.5; N, 8.7; O, 13.3. Found: C, 74.9; H, 3.4; N, 8.8; O, 12.8.

This compound showed infrared absorption at 2.95 and 3.04 μ. It was recovered unchanged (elemental and infrared analysis) after being stirred for 2 hr. in potassium hydroxide and diethylene glycol monoethyl ether at 155–160°.

A solution of 0.37 g. (0.77 mmole) of III and 0.11 g. (1.6 (mmoles) of sodium nitrite in 10 ml. conc. sulfuric acid was stirred overnight at room temperature and then for 2.5 hr. at 70–75°. The reaction product was recovered by drowning on ice, filtering, and washing. Digestion with hot aqueous sodium bisulfite, followed by filtration and acidification, gave 2-anthraquinonecarboxaldehyde, m.p. 185–187°.

N,N-Dimethyl-2-anthraquinonecarboxamide 2-anthraquinonylmethylenehydrazone (V). A steady stream of dimethylamine was passed for 4 hr. through a suspension of 0.52 g. (1.04 mmoles) of II in 10 ml. of nitrobenzene in an oil bath at 190°. The solid dissolved, giving a deep red solution. After completion of the reaction, the mixture was cooled, diluted with a little alcohol, and filtered, giving 0.42 g. (79%) of orange product, m.p. 258–60°. It was crystallized from amyl alcohol without change in melting point. It showed no absorption in the 2.9 μ region.

Anal. Calcd. for $C_{32}H_{21}N_3O_4$: C, 75.2; H, 4.1; N, 8.2; O, 12.5. Found: C, 75.0; H, 4.2; N, 8.3; O, 12.7.

N-Methyl-2-anthraquinonecarboxamide 2-anthraquinonylmethylenehydrazone (IV). This was prepared from methylamine in a way exactly similar to that for the corresponding dimethylamino derivative. It crystallized from dimethylformamide as an orange solid, m.p. 329–330°.

Anal. Calcd. for $C_{31}H_{19}N_3O_4$: C, 74.9; H, 3.8; N, 8.5; O, 12.9. Found: C, 74.6; H, 3.9; N, 8.8; O, 12.6. This compound showed infrared absorption at 2.94 and 6.60 μ.

3,5-Bis(2-anthraquinonyl)-4-methyl-s-triazole (VIII). A mixture of 0.24 g. of IV, 0.50 g. potassium hydroxide, and 20 ml. of diethylene glycol monoethyl ether was stirred 1.5 hr. in an oil bath at 145° and 1.5 hr. at 155°. Cooling, dilution with water, and filtration gave 0.16 g. (67%) of buff solid, m.p. 346–349° dec. Crystallization from 25 ml. of dimethylformamide gave 0.11 g. of very pale yellow solid, m.p. 358–360°. This was crystallized from *o*-dichlorobenzene without further change in melting point.

Anal. Calcd. for $C_{31}H_{17}N_3O_4$: C, 75.1; H, 3.4; N, 8.5. Found: C, 75.0; H, 3.4; N, 8.5.

This substance showed no absorption near 2.9 μ, and much weaker absorption at 6.60 μ than the starting material.

3,5-Bis(2-anthraquinonyl)-4-phenyl-s-triazole (IX). A mixture of 1.0 g. (2.0 mmoles) of II, 0.20 ml. (0.20 g.; 2.1 mmoles) of aniline, and 7–8 ml. of nitrobenzene was stirred for 1.5 hr. in an oil bath at 165°. The product was then cooled, filtered, and washed with benzene. Yield, 0.4 g. of orange yellow solid. An additional crop of 0.2 g. was obtained from the mother liquor. The total amount, 0.6 g., represented a 55% yield. It crystallized from diethylene glycol monoethyl ether or *o*-dichlorobenzene as an orange solid, m.p. 373–375° dec.

Anal. Calcd. for $C_{36}H_{19}N_3O_4$: C, 77.5; H, 3.4; N, 7.5; O, 11.6. Found: C, 77.4; H, 3.5; N, 7.5; O, 11.5.

It showed no infrared absorption in the 2.9 and 6.5 μ regions. It was recovered unchanged (melting point and infrared comparison) after being stirred 1.5 hr. in diethylene glycol monoethyl ether and potassium hydroxide at 155°. 3-(2-Anthraquinonyl)-4,5-diphenyl-*s*-triazole[1] behaved similarly.

2,5-Bis(2-anthraquinonyl)-1,3,4-oxadiazole (X). A mixture of 0.50 g. of 1,2-bis(2-anthraquinonecarbonyl)hydrazine[1] and 5 ml. of polyphosphoric acid was stirred in an oil bath at 175–180° for 4 hr., cooled, diluted, and filtered. The product was washed neutral and dried. Yield, 0.49 g. of gray solid unmelted at 370°. Crystallization from *o*-dichlorobenzene and then dimethylformamide gave a silvery-buff solid.

Anal. Calcd. for $C_{30}H_{14}N_2O_5$: C, 74.7; H, 2.9; N, 5.8. Found: C, 74.7; H, 2.9; N, 6.1.

Unlike the starting material, this compound showed no absorption at 3.22 and 6.44 μ and only weak absorption at 6.33 μ.

The starting material (0.50 g.) was also cyclodehydrated by stirring for 3.5 hr. at room temperature in 10 ml. of 30% oleum. The product was diluted with sulfuric acid followed by ice, filtered, washed neutral, and dried, giving 0.41 g. of cream-colored solid unmelted at 370°. This was purified in the same way and proved identical by infrared and elemental analysis.

1-Chloro-2-anthraquinonecarboxaldazine (XI). A solution of 11.0 g. (0.041 mole) of 1-chloro-2-anthraquinonecarboxaldehyde[4] in 600 ml. of glacial acetic acid was stirred and refluxed in a 1000-ml. three necked flask. Efficient stirring was necessary. A solution of 1.5 ml. (1.5 g.; 0.025 mole) of 85% hydrazine hydrate in 20 ml. of acetic acid was then added dropwise over a 20-min. period. After being stirred and refluxed 10 min. longer, the yellow product was filtered hot and washed with ethanol. Yield, 10.5 g. (96%), m.p. 313–314° dec. A small specimen was crystallized from nitrobenzene (200 ml. per g.) for analysis; m.p. 317–319°.

Anal. Calcd. for $C_{30}H_{14}Cl_2N_2O_4$: C, 67.2; H, 2.6; Cl, 13.2; N, 5.2. Found: C, 67.0; H, 2.7; Cl, 13.1; N, 5.4.

1-Chloro-2-anthraquinonecarbonyl chloride 1-chloro-2-anthraquinonylmethylenehydrazone (XII). A mixture of 0.70 g. (1.3 mmoles) of XI and 20 ml. of nitrobenzene was heated in an oil bath at 110–115° and subjected to a vigorous stream of chlorine for 6 hr. The internal temperature of the mixture was about 95°. It was then cooled, diluted with a little benzene, and filtered. The bright yellow product was washed with benzene and dried. Yield 0.58 g. (78%), m.p. 269–270° dec. dependent somewhat upon the rate of heating. Crystallization from xylene raised the melting point to about 276–277° dec.

Anal. Calcd. for $C_{30}H_{13}Cl_3N_2O_4$: C, 63.1; H, 2.3; Cl, 18.6; N, 4.9; O, 11.2. Found: C, 62.8; H, 2.4; Cl, 18.2; N, 5.0; O, 11.3.

A solution of 0.24 g. of this compound in 2.0 ml. of conc. sulfuric acid was stirred at 125° for 2.5 hr. and then cooled and drowned on ice. The yellow product was filtered and washed. Digestion in warm dilute ammonium hydroxide, followed by filtration and acidification of the filtrate, gave 0.08 g. of very pale yellow 1-chloro-2-anthraquinonecarboxylic acid, m.p. 273–275°, unaffected by admixture with an authentic specimen. Identification was confirmed by infrared comparison.

The ammonia-insoluble fraction was freed from traces of aldehyde by digestion with warm dilute sodium bisulfite solution, leaving 0.12 g. of yellow product m.p. 292–295°. Crystallization from 20 ml. of nitrobenzene gave 0.05 g. of 1-chloro-2-anthraquinonecarboxaldazine (XI), m.p. 311–311½°, unaffected by admixture with an authentic specimen. Identification was confirmed by infrared comparison.

1-Chloro-2-cyanoanthraquinone (VII). A steady stream of chlorine was passed for 15 min. through a mixture of 0.30 g. (0.57 mmole) of 1-chloro-2-anthraquinonecarboxaldazine

(XI) and 5 ml. of *o*-dichlorobenzene heated in an oil bath at 155°. A clear solution was obtained after 5 min. A yellow solid separated on cooling; this was filtered and washed with benzene; yield, 0.20 g. (67%), m.p. 247–250°, raised to 248–251° on crystallization from toluene. By mixed melting point and infrared comparison, this was identical with an authentic sample.

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[CONTRIBUTION FROM THE DEPARTMENTS OF SURGERY AND CHEMISTRY, SINAI HOSPITAL OF BALTIMORE, INC., AND THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND, AND THE DEPARTMENT OF PATHOLOGY, UNIVERSITY OF LONDON, ENGLAND.]

Preparation of Nitrotetrazolium Salts Containing Benzothiazole[1]

SHANKAR S. KARMARKAR, A. G. EVERSON PEARSE, AND ARNOLD M. SELIGMAN

Received September 30, 1959

In order to take advantage of the favorable influence for histochemistry of the *p*-nitrophenyl group at *N*-2 and the potential of chelating heavy metals by the thiazole-(2) group at *N*-3 in tetrazolium salts, a variety of mono and ditetrazolium salts incorporating these features were prepared. The simplest analogue (II) was found to chelate well and was reduced readily by dehydrogenase systems of mammalian tissues. Its redox potential was close to that of INT and Nitro-BT. The benzothiazole-(2) group in the C-5 position did not participate in chelation.

The discovery that a *p*-nitro group in the *N*-2 phenyl ring of tetrazolium salts confers favorable properties on the readiness with which they accept hydrogen from various dehydrogenase systems[2,3] and the discovery that a formazan containing a dimethylthiazole group at the N-3 position (MTT) chelates well with cobalt,[4,5] suggested to us that it would be worthwhile to prepare N-3 and C-5 benzothiazole derivatives of tetrazolium salts containing in addition a *p*-nitrophenyl group at N-2. It was also hoped that the remarkable substantive properties for protein in histochemical methodology[6] exhibited by Nitro-BT [2,2′-di-*p*-nitrophenyl-5,5′-diphenyl-3,3′-(3,3′-dimethoxy-4,4′-biphenylene) ditetrazolium chloride] could be duplicated in benzothiazole analogues of dinitroditetrazolium salt. Although Nitro-BT and a 5-*m*-iodophenyl analogue of Nitro-BT have been used to demonstrate dehydrogenases with electron microscopy,[7] there should be an advantage to using nitrotetrazolium salts that yield formazans of high substantivity and capable of chelating metals of high atomic number. The development of such agents should make possible precise intramitochondrial localization of dehydrogenase activity with the electron microscope. For this purpose benzothiazole groups were introduced into the N-3 and C-5 positions and *p*-nitrophenyl groups were placed at N-2. Ditetrazolium salts were also prepared with benzothiazol and *p*-nitrophenyl groups, related to BT and Nitro-BT.

The formazan (I) was obtained by coupling *p*-nitrobenzene diazonium chloride with benzothiazolylhydrazone-(2) of benzaldehyde in the presence of alkali. Attempts to prepare I by coupling diazotized 2-aminobenzothiazole with *p*-nitrophenylhydrazone of benzaldehyde failed. Oxidation of I with *N*-bromosuccinimide in ethyl acetate[8] gave the tetrazolium bromide, which was converted to the corresponding chloride (II) by treatment with silver chloride. Oxidation of I with isoamyl nitrite and glacial acetic acid resulted in the formation of a tetrazolium salt (III) containing two nitroso groups.[9] Attempts to remove these nitroso groups with ethanolic hydrochloric acid[9] resulted in the formation of IV which did not react like a tetrazolium salt.

Similarly, benzothiazolylhydrazone-(2) of benzothiazole-2-aldehyde[10] on treatment with *p*-nitrobenzene diazonium chloride gave a formazan (V), which on oxidation with *N*-bromosuccinimide in ethyl acetate gave a tetrazolium bromide which was converted with silver chloride to the corresponding tetrazolium chloride (VI). Oxidation of V with isoamyl nitrite and glacial acetic acid gave a nitroso derivative (VII) which on treatment

(1) This investigation was supported by a research grant (CY-2478) from the National Cancer Institute, National Institutes of Health, Department of Health, Education, and Welfare, Bethesda, Maryland.

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