

Insofar as the present study is concerned the question of the mechanism of charge transfer (*e.g.*, hyperconjugation) does not enter. However, the transfer is long-range, *i.e.*, to atoms more than one bond removed from the substituent carbon. The distribution of the methyl effect at the various ring positions permits a discussion of conjugation that is in many respects more detailed and possibly less circuitous than those based on composite molecular properties.

Possible effects due to ring currents in the heterocyclic compounds studied here have not been considered in detail. It seems reasonable to suppose that these have been largely cancelled by the use of

shift differences, provided that any existing ring current will not be greatly modified by methyl substitution.

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The Structure of Dehydrodithizone: A Novel Synthesis of Tetrazolium Salts¹

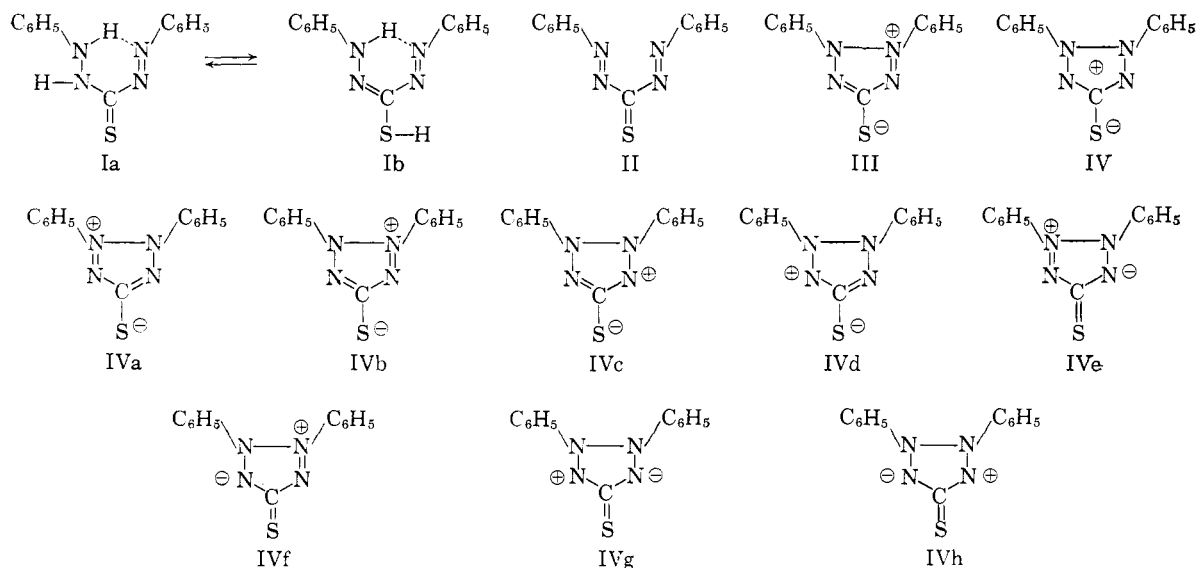
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A nucleophilic displacement of halogens from alkyl halides by dehydrodithizone with concomitant tetrazolium salt formation has been demonstrated. These displacement reactions represent a novel synthesis of a new class of tetrazolium salts, and they also provide chemical evidence in support of the cyclic "meso-ionic" structure proposed for dehydrodithizone in this paper. In addition, the *pK'* values for two of the compounds described have been determined, and these values offer additional support for the cyclic "meso-ionic" structure of dehydrodithizone.

Dithizone, 1,5-diphenylthiocarbazon (Ia,b), is readily oxidized to an orange crystalline dehydro form^{3,4} for which two structures have been proposed. Probably the most commonly accepted structure for dehydrodithizone is the 1,5-diphenyl-

was based predominantly upon the physical properties of the compound. More recently the tetrazolium betaine structure has received support from the ultraviolet spectroscopic studies of Grammaticakis.⁶ Further support for a structure similar



thiocarbazon structure II which was first proposed by E. Fischer.³ The tetrazolium betaine structure III was later proposed by Bamberger and co-workers.⁵ Their proposal of a betaine structure

to III based on the chemical properties of dehydrodithizone will be presented in this paper. Since, in many respects, dehydrodithizone resembles the sydnone, and the charges may be considered to be delocalized due to contributions from IV(a-h) to the resonance hybrid, it is suggested that IV better represents its structure than III.

(1) Taken in part from the doctoral dissertation of James W. Ogilvie, The Johns Hopkins University, 1955.

(2) (a) Procter and Gamble Fellow, 1953; du Pont Fellow, 1954. (b) Department of Physiological Chemistry, The Johns Hopkins University School of Medicine, Baltimore 5, Md.

(3) E. Fischer and A. Besthorn, *Ann.*, **212**, 316 (1882).

(4) H. Fischer, *Angew. Chem.*, **50**, 919 (1937).

(5) E. Bamberger, R. Padova and E. Ormerod, *Ann.*, **446**, 280 (1926).

(6) P. Grammaticakis, *Compt. rend.*, **234**, 528 (1952).

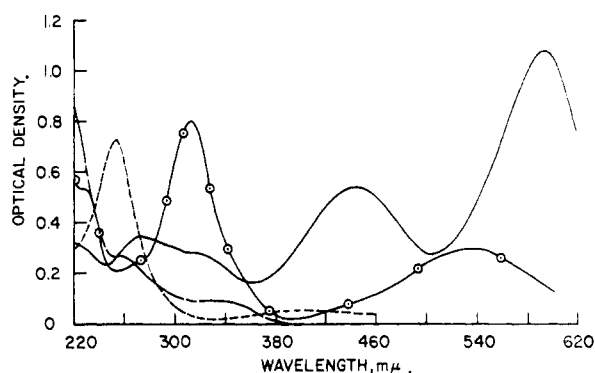


Fig. 1.—Ultraviolet and visible absorption spectra of 3.42×10^{-5} M dithizone (—), 3.0×10^{-5} M dehydrodithizone (---), 3.0×10^{-5} M isomeric dehydrodithizone (—○—○—), and 3.0×10^{-5} M 5-methylmercapto-2,3-diphenyltetrazolium iodide (----). All solutions in 95% ethyl alcohol.

This representation of dehydrodithizone as in IV utilizes the now accepted symbolism for meso-ionic compounds and does not imply that a unit negative charge is associated with the exocyclic sulfur atom.⁷ Structures IVa and IVb would be expected to be the major contributors if the structure were truly a betaine, as proposed by Bamberger; however, evidence will be presented which supports considerable, and perhaps even major, contributions by such structures as IV(e-f) to the resonance hybrid. Henry and co-workers⁸ have also proposed that certain tetrazoles such as the 1,3-dialkyl-5-iminotetrazoles and the 2-methyl-5-alkylamino-tetrazoles are "meso-ionic" compounds, and they have used the following symbolism.

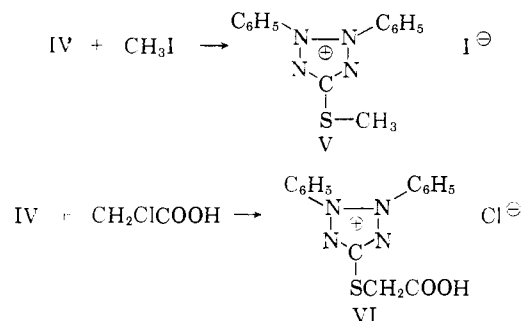


The physical properties of dehydrodithizone are better explained *via* IV than II. Thus dehydrodithizone is more soluble than dithizone in polar solvents, such as an aqueous alcohol solution, as a consequence of its more polar nature. Dehydrodithizone in 95% ethanol possesses only a weak broad absorption band in the visible region at 400 mμ as contrasted to dithizone which is an intensely colored material with maxima at 446 mμ and 595 mμ in 95% ethanol (Fig. 1). A decrease in the light absorption in the visible region upon oxidation is characteristic of the oxidation of formazans to tetrazolium salts. Dehydrodithizone in 95% ethanol has a strong absorption band in the ultraviolet at 254 mμ (Fig. 1) which is similar to that reported for other "meso-ionic" tetrazoles by Henry and co-workers.⁸ Moreover, the chemical reactions of dehydrodithizone are consistent with structure IV. The high electron density around the sulfur atom resulting from contributions from IV(a-d) and/or the high polarizability of such a molecule should bestow nucleophilic properties upon the sulfur atom. Support for the nucleophilic

(7) W. Baker and W. D. Ollis, *Quart. Revs.*, **11**, 15 (1957).

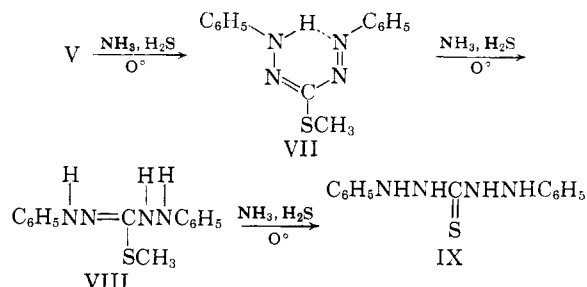
(8) R. A. Henry, W. G. Finnegan and E. Lieber, *J. Am. Chem. Soc.*, **76**, 2894 (1954).

nature of the sulfur was obtained in the following displacement reactions on carbon.



These displacement reactions proceed very rapidly in chloroform and the water-soluble products formed are true tetrazolium salts which undergo the reactions typical of tetrazolium salts such as reductions to formazans. These reductions have been carried out with NH_3 and H_2S , with an alkaline solution of a reducing sugar, and enzymically by a rat liver homogenate. Dehydrodithizone, although not a true tetrazolium salt, is reduced under these same conditions to dithizone, which in the enol form (Ib) is a formazan. Similar nucleophilic displacement reactions have been reported for other meso-ionic compounds.⁹⁻¹¹

The reduction of V by NH_3 and H_2S at 0° in ethanol proceeds through several isolable intermediate compounds. The first product of the reduction is S-methyldithizone (VII) which separates as a red precipitate.



Compound VII is identical with S-methyldithizone prepared by the direct methylation of an alkaline solution of dithizone^{12,13} with dimethyl sulfate as shown by its melting point and ultraviolet and visible spectrum. However, if the reduction is allowed to continue without isolating the S-methyldithizone, the red precipitate redissolves, and a white crystalline precipitate forms which is readily reoxidized to S-methyldithizone. Therefore, the white crystalline product has been assigned the structure VIII. If compound VIII is not isolated immediately, but instead is allowed to stand in the alcoholic ammonium sulfide solution for 4 hours, it is converted to 1,5-diphenylthiocarbazine IX, which was identified

(9) A. Schönberg, *J. Chem. Soc.*, 824 (1938).

(10) L. L. Bambas, "The Chemistry of Heterocyclic Compounds," Vol. IV, Weissberger, ed., New York, N. Y., 1952, p. 202.

(11) M. Busch, W. Kamphausen and S. Schneider, *J. prakt. Chem.*, **67**, 222 (1903).

(12) I. S. Bhatia, Dissertation, The Johns Hopkins University, 1949.

(13) H. M. Irving and C. F. Bell, *Nature*, **168**, 756 (1952).

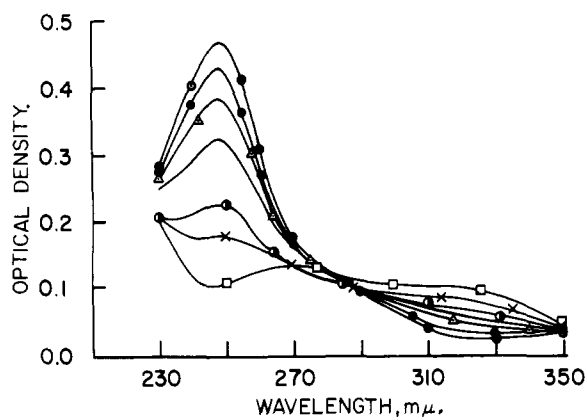
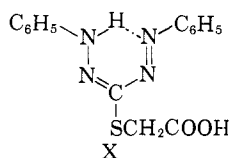


Fig. 2.—Ultraviolet absorption spectra of $2.0 \times 10^{-5} M$ dehydrodithizone: in H_2O , $-\circ-\circ-$; in $2.0 N HCl$, $-\bullet-\bullet-$; in $3.0 N HCl$, $-\triangle-\triangle-$; in $4.0 N HCl$, $-\square-\square-$; in $5.0 N HCl$, $-\circ-\circ-$; in $5.7 N HCl$, $-\times-\times-$; in $7.7 N HCl$, $-\square-\square-$. All solutions contain 0.5% ethyl alcohol.

by its melting point and by its electrolytic oxidation to dithizone. This conversion of VIII to IX probably represents the nucleophilic displacement of CH_3S^\ominus by HS^\ominus . A similar displacement of halogens from the 3-position in formazans has been reported.^{14,15} Also in the Bamberger synthesis of dithizone,^{5,16,17} the nitroformazyl intermediate is reduced with ammonium sulfide, and the resulting amino group in the 3-position is displaced by HS^\ominus . Compound VI, 5-carboxymethylmercapto-2,3-diphenyltetrazolium chloride, undergoes a similar reductive sequence with ammonium sulfide, and the intermediate formazan thus isolated has the structure X.



The pK_a for the protonated form of dehydrodithizone (XI) has been determined in aqueous solutions of HCl and found to be -1.57 (Figs. 2 and 3). The H_0 values used for the HCl solutions were those given by Paul and Long,¹⁸ and the ratios of the concentration of the protonated to the non-protonated forms were determined spectrophotometrically. The pK_a was determined graphically by the method of Davis and Geissman.¹⁹ The fact that the protonated dehydrodithizone is such a strong acid would appear to support an appreciable contribution to the resonance hybrid from structures such as XII.

In other words, the weak basicity of the non-protonated dehydrodithizone can best be explained by including contributions from structures IVc-h

(14) R. Fusco and R. Romani, *Gazz. chim. ital.*, **76**, 419 (1946).

(15) H. M. Irving and C. F. Bell, *J. Chem. Soc.*, 3538 (1953).

(16) E. Bamberger, *Ber.*, **27**, 155 (1894).

(17) E. Bamberger, O. Schmidt and H. Levenstein, *ibid.*, **33**, 2043 (1900).

(18) M. A. Paul and E. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(19) C. T. Davis and T. A. Geissman, *J. Am. Chem. Soc.*, **76**, 3507 (1954).

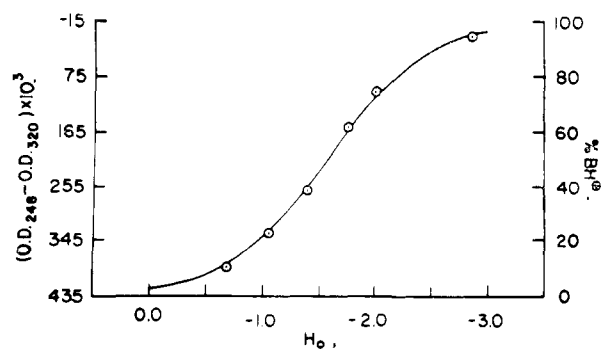
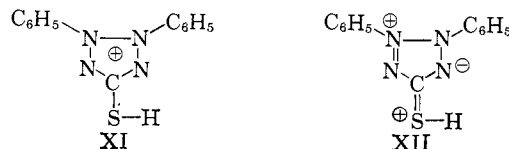
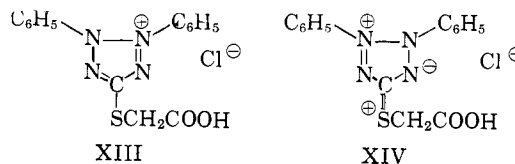


Fig. 3.—Dehydrodithizone: acidity function (H_0) vs. $(O.D._{248} - O.D._{320}) \times 10^3$; points from spectral data; curve calculated for $pK_{BH^\oplus} - 1.57$.

to the resonance hybrid. Spectroscopic evidence indicates the addition of the proton occurs at only one position since an isosbestic point at $280 m\mu$ exists, and the similarity of the spectral change upon protonation to that observed upon alkylation of the sulfur atom of dehydrodithizone suggests that the protonation is occurring on the sulfur atom, as would be expected.



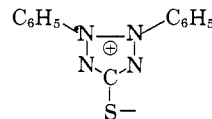
The pK_a' of the carboxyl group of VI has been determined by potentiometric acidimetric titration and found to be 2.47. This large increase in the acidity of the carboxyl group of VI over that of acetic acid is quite surprising in view of the distance of the positive charge from the carboxyl group in contributing structures such as XIII; however, again the observed pK_a' would appear to support the importance of contributions from structures such as XIV in which the positive charge is nearer the carboxyl group.



By use of the Branch and Calvin equation²⁰ it

$$\log K = -4.75 + \frac{A_\alpha \Sigma I_\alpha^{i\alpha}}{1 + B_\alpha \Sigma I_\alpha^{i\alpha}} + \log \frac{n'}{m'}$$

can readily be demonstrated that structures such as XIII cannot be the sole contributors to the resonance hybrid, and that perhaps they may not be even the major contributors. By substituting in the equation the experimentally determined pK_a' of $+2.47$ the net inductive effect (I_α) of substitut-



(20) G. E. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1945, p. 221.

ing for an α -H of acetic acid is $I_\alpha = 9.84$. In structure XIII this I_α would result from the ring substituent single-bonded through sulfur to the α -carbon of the acetic acid. Therefore, the inductive constant of the ring, I_R , can now be calculated for such structures, since $\Sigma I_\alpha^{i\alpha} = I_{\text{sulfur}} + 0.357I_R$. This calculation indicates that $I_R = +18.05$. This is an impossibly large value for I_R since the inductive constant of a full positive charge is only $+12.3$. Therefore, structures involving a charged ring single-bonded through sulfur cannot account for the calculated net inductive effect of the group, and thus structures such as XIV in which the sulfur bears a positive charge must also be assumed to make significant contributions to the resonance hybrid.

The orange colored cyclic dehydrodithizone IV undergoes a rearrangement when heated to 60 – 70° in glacial acetic acid to yield a beautiful reddish-bronze crystalline compound which is isomeric with IV as it yields the same C, H and N values upon analysis. This same compound can be obtained by refluxing dithizone in glacial acetic acid. One possible structure for this rearranged dehydrodithizone is II, the 1,5-diphenylthiocarbodiazone structure. This rearranged dehydrodithizone forms a bluish-purple solution in ethanol, with absorption maxima at 314 and 538μ (Fig. 1). Its solubility properties are compatible with structure II as they are quite similar to those of dithizone. The reduction of this isomeric reddish-bronze dehydrodithizone (XV) to a colorless product or products does occur; however, it is a much slower process than the corresponding reduction of a tetrazolium structure, the reduction does not appear to proceed through an obvious formazan intermediate, and the yield is poor in contrast to the excellent yields which have been obtained in the corresponding reduction of IV. The reduced material has been reoxidized electrolytically to a product which appears to be a mixture of several compounds, and which thus far has proved to be very difficult to separate. The major product of the mixture resulting from the oxidation has been partially purified by chromatography on silica gel and, at this stage of purification, its spectrum is quite similar but not identical to that of dithizone. It also reacts with mercuric ions to yield a chelate whose spectrum again is quite similar but not identical to that of mercury dithizonate. However, since no component of this mixture has been definitely identified, additional work will be required before the structure of the isomeric reddish-bronze dehydrodithizone can be established.

Acknowledgments.—The authors wish to thank Mr. Vernon K. Miyamoto for the determinations of the pK 's presented. J.W.O. also gratefully acknowledges financial aid received from the Hynson, Westcott and Dunning Fund.

Experimental

5-Methylmercapto-2,3-diphenyltetrazolium Iodide (V).—A solution of 0.95 g. (3.75 mmoles) of dehydrodithizone (IV)—prepared by the oxidation of 1,5-diphenylthiocarbazine (IX) by $K_2Fe(CN)_6^{21}$ —and 0.30 ml. (0.68 g., 4.8 mmoles) of CH_3I in 100 ml. of chloroform was refluxed for 1 hour. The chloroform was then distilled off, and the resulting yellow crystalline residue after recrystallization

from an acetone– H_2O solution furnished 1.135 g. of V (76.4% yield), m.p. 203 – 207° dec.

Anal. Calcd. for $C_{14}H_{13}N_4SI$: C, 42.43 ; H, 3.31 . Found: C, 42.58 ; H, 3.60 .

5-Carboxymethylmercapto-2,3-diphenyltetrazolium Chloride (VI).—A solution of 0.95 g. (3.75 mmoles) of IV and 0.473 g. (5.0 mmoles) of chloroacetic acid in 50 ml. of chloroform was refluxed for 1 hour during which the color of the solution changed from red to violet. Upon cooling, a precipitate formed which was white when isolated and washed with chloroform. Recrystallization from 1-propanol gave 1.170 g. (90% yield) of VI, m.p. 216 – 218° dec.

Anal. Calcd. for $C_{15}H_{13}N_4O_2SCI$: C, 51.64 ; H, 3.76 ; neut. equiv., 348.8 . Found: C, 51.19 ; H, 3.74 ; neut. equiv. (by potentiometric titration), 356.5 .

Reduction of 5-Methylmercapto-2,3-diphenyltetrazolium Iodide (V) by Ammonium Sulfide. **Method A.**—A 0.5 -g. sample of V was added to 20 ml. of absolute ethanol in a test-tube in an ice-bath, and NH_3 was passed into the mixture for 30 minutes. Most of V had dissolved at this point to give a yellow solution; H_2S was then introduced for 1 hour during which the solution turned dark red and deposited a red precipitate which subsequently dissolved to give a yellow solution which deposited a white crystalline precipitate. The mixture was removed from the ice-bath and allowed to stand for 4 hours before isolation of the precipitate by filtration. Concentration of the filtrate resulted in a second precipitate identical with the first. Recrystallization of the combined precipitates from ethanol gave 0.30 g. (88% yield) of a white crystalline material which darkened to a light blue-violet color at 115 – 120° and melted with decomposition above 140° —a behavior characteristic of 1,5-diphenylthiocarbazine (IX). The compound was identified as IX by an analysis of the dithizone (I) obtained by electrolytic oxidation (see below for procedure).

Anal. Calcd. for $C_{13}H_{12}N_4S$: C, 60.91 ; H, 4.72 . Found: C, 60.74 ; H, 4.98 .

Method B.—The ammonium sulfide reduction of V was repeated as outlined in method A, and a sample of each intermediate compound was isolated as it formed by filtering only a part of the reaction mixture.

1. The red intermediate was isolated and recrystallized from acetone– H_2O . The reddish-brown crystalline needles which resulted were identified as S-methyldithizone (VII) by mixed m.p.

2. Part of the white crystalline precipitate was isolated as soon as it formed without allowing it to stand in the ammonium sulfide solution. This white crystalline precipitate (VIII) was very unstable when removed from the ammonium sulfide solution and was readily air oxidized back to the red intermediate S-methyldithizone.

Reduction of 5-Carboxymethylmercapto-2,3-diphenyltetrazolium Chloride (VI) by Ammonium Sulfide.—A 0.5 -g. sample of VI was reduced following the procedure outlined above in method A. After standing 4 hours, 0.440 g. (97% yield) of IX was isolated and identified by its melting behavior and by an analysis of the dithizone obtained by electrolytic oxidation.

Anal. Calcd. for $C_{13}H_{12}N_4S$: C, 60.91 ; H, 4.72 . Found: C, 60.62 ; H, 4.92 .

Reduction of 5-Methylmercapto-2,3-diphenyltetrazolium Iodide (V) by an Alkaline Solution of Dextrose.—A solution consisting of 0.10 g. of V, 0.25 g. of dextrose, 5.0 ml. of $0.1 M$ NaOH and 5.0 ml. of ethanol was gently refluxed for 10 minutes in a water-bath, during which the solution color changed from yellow to a deep red and a crystalline precipitate of reddish-brown needles formed. The mixture was cooled and the precipitate was isolated and washed with H_2O . This product, 0.06 g. (88.1% yield), was identified as VII by its m.p. (127 – 129°) and its spectrum in 95% ethanol (λ_{max} 265 , 414 , 535μ) which is identical to that of S-methyldithizone prepared by direct methylation of dithizone.¹²

Reduction of 5-Carboxymethylmercapto-2,3-diphenyltetrazolium Chloride (VI) by an Alkaline Solution of Dextrose.—A solution consisting of 0.250 g. of VI, 0.125 g. of NaOH and 1.0 g. of dextrose in 50 ml. of H_2O was maintained at 80° for 20 minutes and then cooled in an ice-bath. A flocculent red precipitate formed upon the addition of

(21) J. Reinheimer, Dissertation, The Johns Hopkins Univ., 1948.

dilute H_2SO_4 which yielded 0.125 mg. (55.3% yield) of crystalline S-carboxymethyl dithizone (X) when crystallized from benzene. When recrystallized from alcohol-water, X was obtained as long reddish-brown needles, m.p. 150–152° dec.

Anal. Calcd. for $C_{15}H_{14}N_4O_2S$: C, 57.31; H, 4.49. Found: C, 57.00; H, 4.64.

Reduction of Dehydrodithizone (IV) by an Alkaline Solution of Dextrose.—A solution containing 0.200 g. of IV, 0.125 g. of NaOH, 0.75 g. of dextrose, 20 ml. of water and 20 ml. of ethanol was refluxed for 15 minutes, during which the solution changed from light yellow to dark red in color. This red solution was filtered and 50 g. of ice was added to the filtrate. Upon acidification of the cold filtrate with dilute H_2SO_4 , a black precipitate of dithizone (I) formed which was then isolated, washed with water, and dried in a vacuum desiccator. The yield of crude I was 0.180 g. (90%). This crude I was recrystallized from benzene in the form of dark violet-black needles.

Anal. Calcd. for $C_{15}H_{12}N_4S$: C, 60.91; H, 4.72. Found: C, 60.99; H, 4.60.

Electrolytic Oxidation of 1,5-Diphenylthiocarbazine (IX) to Dithizone (I).—The cell used was similar to one described by Allen²² with a platinum electrode substituted for the mercury electrode. The electrolyte consisted of a solution of 2.0 g. of KOH, 70 ml. of H_2O and 130 ml. of acetone. The potential of the working electrode (anode) was maintained constant at -0.2 of a volt with respect to the calomel electrode by varying the potential applied across the anode and cathode by means of a rheostat.

A 5.0-g. sample of IX, prepared by the condensation of phenylhydrazine and CS_2 ,²³ was dissolved in 160 ml. of the electrolyte solution and added to the anode compartment. The cathode compartment was filled with 15 ml. of the electrolyte. The oxidation was carried out with constant stirring and at an oxidation potential 0.2 of a volt negative to the calomel cell. The initial current was 1.5 amp., and after 75 minutes the current had decreased to 0.064 amp., indicating the carbazine was almost completely oxidized. The red solution of the anode compartment was added to a beaker which contained an ice-cold solution of 2 g. of KOH in 130 ml. of water and 25 g. of ice. This solution was acidified in an ice-bath with 40 ml. of 10% H_2SO_4 . A dark precipitate of I formed which was isolated after standing one minute. After drying, this precipitate of crude I weighed 4.80 g. This crude I was redissolved in a solution of 2 g. of NaOH in 150 ml. of H_2O . The small amount of alkaline-insoluble material was removed by filtration and the filtrate acidified in an ice-bath with 2 N H_2SO_4 . The reprecipitated I was removed by filtration and dried. The yield of I by this procedure was 4.40 g. (88.9%).

Rearrangement of Dehydrodithizone (IV).—A 0.5-g. sample of IV in 5 ml. of glacial acetic acid was slowly heated in an oil-bath. At 60–70° the rearrangement began and the solution became dark red. After refluxing for 10 minutes, the solution was cooled and then added to 150 ml. of 50% ethanol. This solution was heated and filtered. Upon cooling, the filtrate deposited 65 mg. of the isomeric dehydrodithizone (XV) in the form of reddish-bronze crystalline needles. Larger yields have been obtained by increasing the time of reflux. Compound XV was purified by chromatography on an alumina column using 1% methanol-benzene to develop the column, and by two recrystallizations from ethanol- H_2O solutions; m.p. 179–180° dec.

Anal. Calcd. for $C_{15}H_{10}N_4S$: C, 61.42; H, 3.93. Found: C, 61.36; H, 4.02.

Preparation of the Isomeric Dehydrodithizone (XV) from Dithizone (I).—A 3.5-g. sample of I in 20 ml. of glacial acetic acid was refluxed for 30 minutes. After cooling, the solution was poured into 150 ml. of distilled H_2O at room temperature with stirring. The precipitate which formed was isolated, washed with H_2O , and dried overnight in a vacuum desiccator. The yield of crude XV was 1.70 g. The crude XV was recrystallized from ethanol-water; m.p. 179–180° dec. The spectrum of this product was iden-

tical with the spectrum of the product obtained by rearrangement of IV in acetic acid.

Anal. Calcd. for $C_{15}H_{10}N_4S$: C, 61.42; H, 3.93; N, 22.04. Found: C, 61.46; H, 4.03; N, 21.73.

Ammonium Sulfide Reduction of the Isomeric Dehydrodithizone (XV).—A 0.9-g. sample of XV, which had been purified by chromatography on alumina and by two recrystallizations from ethanol-water, was added to 30 ml. of absolute alcohol and reduced with ammonium sulfide at 0° as described above. This reduction occurred much more slowly than the corresponding reduction of IV, and did not obviously pass through a formazan intermediate. After standing overnight at room temperature in the ammonium sulfide solution, approximately one-third of the ethanol was removed *in vacuo* and the white precipitate isolated and dried. The yield of reduced material was 0.350 g., m.p. 135–140° dec. This reduced material did not darken as much as does IX upon heating; however, it did dissolve in an alkaline solution to yield a red solution which formed a dark flocculent precipitate when acidified. This dark precipitate displayed an activity toward the heavy metals similar to that of dithizone.

A 0.325-g. sample of the reduced material was oxidized electrolytically as described above for IX. The black oxidized product was isolated, washed, and dried at 50°; yield 0.250 g. A benzene solution of this oxidized product was chromatographed on a silica gel column, using benzene to develop the column. Partial purification was obtained by the removal of a yellow forerun and by the removal of a red impurity which remained on the column. The spectrum of the green benzene eluate which contained a major component of the oxidized material was very similar to the spectrum of dithizone in benzene, but the two spectra were not identical. The mercury chelate of the oxidized material was prepared by adding $HgCl_2$ to a benzene solution of the material, and the resulting reddish-yellow solution was chromatographed on alumina, using a 2% methanol-benzene solution to develop the column. The mercury chelate chromatographed as a sharp well-defined red band which is identical to the chromatographic behavior of mercury dithizonate. Again the spectra of the mercury chelate of the oxidized material and of mercury dithizonate were found to be very similar but not identical. The problem of the spectral differences, and whether or not they are due to impurities, is still unresolved.

Determination of the pK_{BH}^+ of Dehydrodithizone (IV).—The normalities of the HCl solutions were determined by the titration of diluted aliquots with standard base. The solutions were prepared by the addition of 0.5 ml. of a 4×10^{-3} M solution of IV in 95% ethanol to the calculated amount of a standardized HCl solution followed by dilution to 100 ml. with distilled water. The ultraviolet spectrum of each solution was obtained with a Beckman DU spectrophotometer (Fig. 2). The pK_{BH}^+ was determined graphically by the method of Davis and Geissman¹⁹ and found to be -1.57 (Fig. 3). The H_0 values used were those given by Paul and Long.¹⁸ The spectra of five of the seven solutions displayed an isosbestic point at 280 $m\mu$. The spectra of the other two solutions were slightly low at the isosbestic point. Since these two solutions were of intermediate values in HCl concentrations, it is felt that the failure of these two solutions to cross at 280 $m\mu$ was due to experimental error in the preparation of the solutions. A correction for this error was not made because it was so small in magnitude.

Determination of the pK' of 5-Carboxymethylmercapto-2,3-diphenyltetrazolium Chloride (VI).—A 272.73-mg. (0.782 mmole) sample of VI which had been recrystallized from 1-propanol was dissolved in 20 ml. of distilled water and titrated with standard 0.1068 N NaOH which had been prepared in CO_2 -free water. A glass electrode which had been standardized at pH 4 with Beckman pH 4 buffer was used with a Leeds and Northrup model 7664 pH meter. The titration was carried out under nitrogen with constant stirring by a magnetic stirrer except during the actual pH measurements. The pK' , as determined by the pH at half neutralization, was 2.47. The requirement of 0.765 mmole of NaOH to neutralize the sample yields an experimental neutralization equivalent weight of 356.5 g.; calcd. neut. equiv., 348.8 g.

(22) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, p. 34.

(23) J. H. Billman and E. S. Cleland, *Org. Syntheses*, **25**, 38 (1945).