Azo Coupling of Benzenesulfonylhydrazones of Heterocyclic Aldehydes

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The reaction of aldehyde phenylsulfonylhydrazones (VII-XI) with diazotized aromatic and heterocyclic primary amines gave the tetrazoles (XIV-XIX). The yield of the tetrazoles was found to depend to some extent on the nature of the substituent present in the aldehyde moiety. The structures of the tetrazoles obtained was established on the basis of their analytical and spectral data. A tentative explanation for their formation is proposed. The acid dissociation constants of the tetrazoles (XIV) were also determined.

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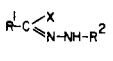
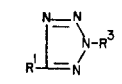
The most generally applicable method for the synthesis of triaryl formazans (I, $R^1 = R^2 = R^3 = Ar$) (Scheme 1) is the coupling of diazonium salts with arylhydrazone derivatives of aldehydes (II) or glyoxalic acid (III) in the presence of alkali, pyridine or sodium acetate (1). Further, it has been reported that arenesulfonylhydrazones (IV) can generate a diazo intermediate upon base treatment, and this behaviour is the basis of pyrazole formation from α,β-unsaturated aldehyde *p*-toluenesulfonylhydrazones (2). By analogy, 5-arenesulfonylformazans (I, $R^2 = SO_2Ar$) are expected to generate arylazoaryldiazomethane when treated with a base. The latter is the analogue of vinyldiazomethane which is known to undergo 1,5-dipolar cyclization to give 3,5-disubstituted pyrazoles (3). Accordingly, the arylazoaryldiazomethane generated from (I, $R^2 = SO_2Ar$) can be expected to undergo similar reaction to afford 2,5-disubstituted tetrazoles (V), or alternatively, can loose nitrogen to give a nitrile imine intermediate that dimerizes to the corresponding 1,4-dihydro-1,3,4,6-tetraaryl-1,2,4,5-tetrazine (VI) (Scheme 1).

Scheme 1

I



II R^1 = alkyl, aryl; R^2 = Ar; X = H
III $R^1 = R^2$ = Ar; X = COOH
IV R^1 = aryl; $R^2 = SO_2Ar$; X = H



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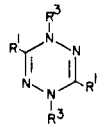
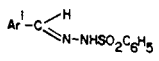
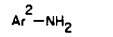


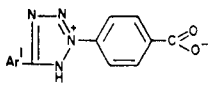
VI



VII Ar^1 = substituted phenyl
VIII Ar^1 = 2-furyl
IX Ar^1 = 2-thienyl
X Ar^1 = 3-pyridyl
XI Ar^1 = 4-pyridyl



XII Ar^2 = substituted phenyl
XIII Ar^2 = 3-pyridyl



XX

In this work, the results of the study of the reaction of two series of aldehyde phenylsulfonylhydrazones, namely, VII-XI with diazotized aromatic (XII) and heterocyclic (XIII) primary amines (Scheme 1) are described. Compounds of series VII to XI were prepared in a rigorously similar manner by treatment of the appropriate aldehyde with phenylsulfonyl hydrazine in ethanol (4,5). The structures of the newly prepared compounds were confirmed by elemental (Table 1) and spectral analyses. Thus, the ir spectra showed absorption bands at 3180-3220 (NH), 1330-1335 and 1160-1170 cm^{-1} ($-SO_2C_6H_5$). Their electronic absorption spectra were those of typical hydrazones (6).

Treatment of compounds of series VII with an equivalent amount of diazotized *p*-aminobenzoic acid (XII, Ar^2 = 4-$HOOCC_6H_4$) in pyridine at 0-5° afforded 2-(*p*-carboxyphenyl)-5-aryltetrazoles (XIV) (Table II). When the reaction was repeated in ethanolic sodium hydroxide or sodium acetate, the tetrazoles (XIV) were also obtained but in much lower yields (see Experimental). Similar treatment of the other heterocyclic aldehyde phenylsulfonylhydrazones (VIII-XI) with the appropriate diazonium salt, prepared from XII and XIII in pyridine, resulted in the formation of the corresponding tetrazole derivatives, namely: 2-aryl-5-(2-furyl)tetrazoles (XV), 2-aryl-5-(2-thienyl)tetrazoles (XVI), 2-aryl-5-(3-pyridyl)tetrazoles (XVII), 2-aryl-5-(4-pyridyl)tetrazoles (XVIII), and 2-(3-pyridyl)-5-aryltetrazoles (XIX) (Table 2). In general, the yields of the tetrazoles are high and was found to depend to some extent on the nature of the substituent in the aldehyde moiety and/or the heterocyclic reside. For example, the yields of (XIVc, Ar^1 = 4-$MeOC_6H_4$; Ar^2 = 4-$HOOCC_6H_4$) and (XIVd, Ar^1 = 4-ClC_6H_4; Ar^2 = 4-$HOOCC_6H_4$) were 40% and 75%, respectively. Also, the yields of series XV to XIX were found to increase in the order 2-thienyl > 2-furyl > 3-pyridyl.

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Table I

Heterocyclic Aldehyde Phenylsulfonylhydrazones (VIII-XI)

Ar^1-CH=NNHSO$_2$C$_6$H$_5$

Compound	Ar^1	Yield %	M.p. °C	Formula	Calcd. % C	H	N	S	Found % C	H	N	S
VIII	2-Furyl	65	142-144	$C_{11}H_{10}N_2O_3S$	52.79	4.04	11.20	12.81	52.70	4.03	11.30	12.75
IX	2-Thienyl	60	138-139	$C_{11}H_{10}N_2O_2S_2$	49.60	3.79	10.52	24.08	49.55	3.78	10.70	24.15
X	3-Pyridyl	70	167-168	$C_{12}H_{11}N_3O_2S$	55.16	4.24	16.08	12.27	55.22	4.22	16.11	12.32
XI	4-Pyridyl	50	136-138	$C_{12}H_{11}N_3O_2S$	55.16	4.24	16.08	12.27	55.30	4.20	16.20	12.30

The structure of the tetrazoles of series XIV to XIX was substantiated from analytical and spectral data (Table II). The electronic absorption spectra of the compounds prepared were of typical 2,5-disubstituted tetrazoles. The absorption pattern in ethanol was characterized by the presence of two or three intense (log $\epsilon > 4$) absorption maxima. The position of such maxima seem to depend on the nature of the groups at positions 2 and 5 of the tetrazole ring. This dependence can be seen by examining the long wavelength maxima of the compounds depicted in Table II.

Examination of the structures of all the tetrazoles prepared indicated that they have cross-conjugated structures, and thus there is no direct electronic interaction between the 2- and 5-substituents. In this respect their spectral characteristics will be similar to that of unsubstituted tetrazoles. This similarity is obvious when the spectra of, for example, 2-phenyl-5-(2-thienyl)tetrazole (XVIa) and 5-(2-thienyl)tetrazole are compared. The latter monosubstituted tetrazole exhibits two maxima in ethanol at 270 and 225 nm (7). The maximum near 270 nm is attributed to the π-π^* transition in the tetrazole ring. Besides, the bathochromic shift exhibited by the maximum of 2-(*p*-carboxyphenyl)-5-substituted aryl tetrazoles (XIVa, XVe, XVId, XVIIf and XVIIIf) as compared with the corresponding 2-phenyl-5-substituted analogues (Table III) can be rationalized in terms of the stabilizaiton of the transition state by its conversion into the zwitterion (XX) (Scheme 1).

That the 2,5-tetrazole bridge acts as an insulator is also substantiated by the independence of the p*K*a values of the tetrazoles (XIVa-f) on the nature of the ring-substituents at the C_5 atom. The acid dissociation constants of the tetrazoles (XIVa-f) were determined (Table IV) potentiometrically in a 50% volume methoxyethanol-water solution at 25.0 ± 1° and μ of 0.10. The values of the p*K*a data indicated that the effect of the substituent in the 5-aryl moiety has negligible influence on the dissociation of the carboxylic group. On the other hand, the p*K*a values of substituted biphenylcarboxylic acid were reported (8) to be correlated by the equation p*K*a = 0.37 + 5.66.

In the ir spectra, the absorptions due to the 2- and 5-positions of the tetrazoles prepared were in accordance with the structures assigned. All the compounds exhibited absorption at 1265-1295 cm^{-1} assignable to the cyclic N-N=N group in analogy with other tetrazoles and triazoles (9). Other characteristic bands near 1070, 1015, and 990 cm^{-1} were observed in most of the spectra. These bands are undoubtedly due to the tetrazole ring system. It has been reported that tetrazole (10), 5-substituted tetrazoles (10), and 1,5-disubstituted tetrazoles (11) show absorptions in the 1100 to 990 cm^{-1} range which were assigned to the tetrazole ring system.

To account for the formation of the tetrazoles from the

Scheme 2

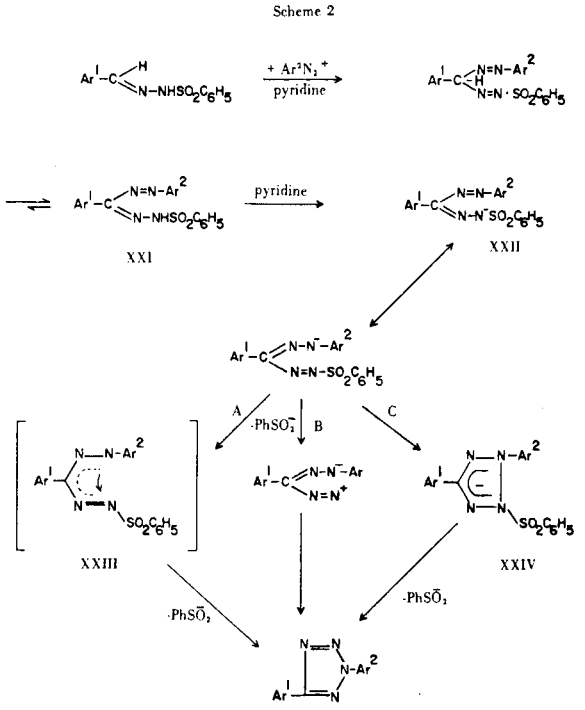
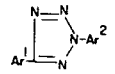


Table II

2,5-Disubstituted Tetrazoles (XIV-XIX)



Compound	Ar^1	Ar^2	Yield %	M.p. °C	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N	λ max (Ethanol) (Log ε) nm
XIVa	C_6H_5	4-$HOOCC_6H_4$	70	>350	$C_{14}H_{10}N_4O_2$	63.15	3.79	21.04	63.03	3.84	21.47	288 (4.05); 279 (4.04); 233 (3.97)
XIVb	4-MeC_6H_4	4-$HOOCC_6H_4$	80	>350	$C_{15}H_{12}N_4O_2$	64.28	4.31	19.99	63.86	4.45	20.29	293 (4.15); 280 (4.12); 242 (4.13)
XIVc	4-$MeOC_6H_4$	4-$HOOCC_6H_4$	40	>350	$C_{15}H_{12}N_4O_3$	60.81	4.08	18.91	60.84	4.08	19.10	303 (4.37); 281 (4.40); 252 (4.46)
XIVd	4-ClC_6H_4	4-$HOOCC_6H_4$	75	>350	$C_{14}H_9ClN_4O_2$	55.92	3.02	18.63	55.84	3.06	18.86 (a)	292 (4.37); 278 (4.39); 243 (4.27)
XIVe	4-BrC_6H_4	4-$HOOCC_6H_4$	65	>350	$C_{14}H_9BrN_4O_2$	48.72	2.62	16.23	48.50	2.60	16.40 (b)	293 (4.46); 278 (4.48); 247 (4.34)
XIVf	4-$NO_2C_6N_4$	4-$HOOCC_6H_4$	60	>350	$C_{14}H_9N_5O_4$	54.02	2.91	22.50	53.96	2.92	22.64	295 (4.46)
XIVg	3-$NO_2C_6H_4$	4-$HOOCC_6H_4$	55	>350	$C_{14}H_9N_5O_4$	54.02	2.91	22.50	53.96	2.92	22.64	275 (4.50); 233 (4.35)
XIVh	4-HOC_6H_4	4-$HOOCC_6H_4$	60	>350	$C_{14}H_{10}N_4O_3$	59.57	3.57	19.85	60.24	4.08	19.70	304 (4.05); 279 (4.10); 253 (4.19)
XIVi	4-$Me_2NC_6H_4$	4-$HOOCC_6H_4$	40	>350	$C_{16}H_{15}N_5O_2$	62.13	4.90	22.64	62.06	5.20	22.45	334 (4.15); 302 (4.34); 288 (4.36); 260 (4.27)
XVa	2-Furyl	C_6H_5	50	82-83	$C_{11}H_8N_4O$			26.40			26.31	285 (4.28); 250 (4.31)
XVb	2-Furyl	4-MeC_6H_4	55	106-107	$C_{12}H_{10}N_4O$			24.77			24.60	287 (4.29); 252 (4.27)
XVc	2-Furyl	4-$MeOC_6H_4$	40	93-94	$C_{12}H_{10}N_4O_2$			23.13			22.95	293 (4.35); 257 (4.21)
XVd	2-Furyl	4-ClC_6H_4	50	120-122	$C_{11}H_7ClN_4O$			22.77			23.10 (c)	300 (4.27); 252 (4.38)
XVe	2-Furyl	4-$HOOCC_6H_4$	55	>250	$C_{12}H_8N_4O_3$			20.87			20.98	295 (4.37); 250 (4.32)
XVIa	2-Thienyl	C_6H_5	60	130-132	$C_{11}H_8N_4S$			24.55			24.67 (d)	285 (4.30); 250 (4.13)
XVIb	2-Thienyl	4-MeC_6H_4	65	95-97	$C_{12}H_{10}N_4S$			23.12			23.33 (e)	290 (4.32); 250 (4.13)
XVId	2-Thienyl	4-$HOOCC_6H_4$	60	228-230	$C_{12}H_8N_4O_2S$			20.58			21.02 (g)	302 (4.56); 250 (4.23)
XVIIa	3-Pyridyl	C_6H_5	35	138-138	$C_{12}H_9N_5$			31.38			31.50	277 (4.32); 267 (4.33)
XVIIb	3-Pyridyl	4-MeC_6H_4	30	102-103	$C_{13}H_{11}N_5$			29.52			29.20	280 (4.33); 270 (4.33)
XVIIe	3-Pyridyl	4-$NO_2C_6H_4$	40	190-192	$C_{12}H_8N_6O_2$			31.33			31.69	295 (4.36); 237 (4.10)
XVIIf	3-Pyridyl	4-$HOOCC_6H_4$	50	>300	$C_{13}H_9N_5O_2$			26.21			26.01	283 (4.29); 272 (4.26)
XVIIg	3-Pyridyl	3-Pyridyl	40	143-145	$C_{11}H_8N_6$			37.48			37.72	279 (4.26); 268 (4.25)
XVIIIa	4-Pyridyl	C_6H_5	40	146-147	$C_{12}H_9N_5$			31.37			31.33	270 (4.39)

Table II (continued)

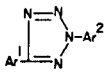
2,5-Disubstituted Tetrazoles (XIV-XIX)

Compound	Ar^1	Ar^2	Yield %	M.p. °C	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N	λ max (Ethanol) (log ε) nm
XVIIIb	4-Pyridyl	4-MeC_6H_4	50	142-143	$C_{13}H_{11}N_5$			29.52			29.71	275 (4.21)
XVIIIc	4-Pyridyl	4-MeOC_6H_4	40	162-163	$C_{13}H_{11}N_5O$			27.65			28.13	290 (4.66)
XVIIId	4-Pyridyl	4-ClC_6H_4	70	150-152	$C_{12}H_8ClN_5$			27.18			27.68 (h)	277 (4.66)
XVIIIe	4-Pyridyl	$4\text{-NO}_2C_6H_4$	60	172-174	$C_{12}H_8N_6O_2$			31.33			30.87	290 (4.38)
XVIIIg	4-Pyridyl	3-Pyridyl	50	149-151	$C_{11}H_8N_6$			37.48			37.51	272 (4.42)
XIXa	C_6H_5	3-Pyridyl	50	128-129	$C_{12}H_9N_5$			31.37			31.42	286 (4.19); 277 (4.20); 235 (4.21)
XIXb	4-MeC_6H_4	3-Pyridyl	40	113-114	$C_{13}H_{11}N_5$			29.52			29.61	290 (4.21); 276 (4.24); 240 (4.31)
XIXc	4-MeOC_6H_4	3-Pyridyl	40	159-160	$C_{13}H_{11}N_5O$			27.65			27.48	300 (4.21); 281 (4.32); 251 (4.36)
XIXd	4-ClC_6H_4	3-Pyridyl	50	137-138	$C_{12}H_8ClN_5$			27.18			27.11	291 (4.23); 276 (4.30); 247 (4.21)
XIXe	4-BrC_6H_4	3-Pyridyl	45	145-147	$C_{12}H_8BrN_5$			23.18			23.10	291 (4.24); 276 (4.37); 252 (4.30)
XIXf	$4\text{-NO}_2C_6H_4$	3-Pyridyl	50	175-176	$C_{12}H_8N_6O_2$			31.33			31.51	289 (4.62)
XIXg	4-HOC_6H_4	3-Pyridyl	50	212-214	$C_{12}H_9N_5O$			29.28			29.22	302 (4.39); 280 (4.52); 251 (4.61)

(a) Cl %: Calcd.: 11.79; Found: 11.60. (b) Br %: Calcd.: 23.15; Found: 23.05. (c) Cl %: Calcd. 14.38; Found: 14.42. (d) S %: Calcd.: 14.00, Found: 13.89. (f) S %: Calcd.: 13.23; Found: 13.18. (f) s%: Calcd.: 12.41; Found; 12.55. (g) S%: Calcd.: 11.78; Found: 11.87. (h) Cl%: Calcd.: 13.76; Found: 13.90.

Table III

Bathochromic Shift in the Electronic Spectra of Some Tetrazoles



Compound	Ar^1	Ar^2	λ max (Ethanol) (Log ε) nm	Δλ
	C_6H_5	C_6H_5	272 (4.26) (a)	
XIVa	C_6H_5	4-$HOOCC_6H_4$	288 (4.05)	16
XVa	2-Furyl	C_6H_5	285 (4.28)	
XVe	2-Furyl	4-$HOOCC_6H_4$	295 (4.37)	10
XVIa	2-Thienyl	C_6H_5	285 (4.30)	
XVId	2-Thienyl	4-$HOOCC_6H_4$	302 (4.56)	17
XVIIa	3-Pyridyl	C_6H_5	277 (4.32)	
XVIIf	3-Pyridyl	4-$HOOCC_6H_4$	283 (4.29)	6
XVIIIa	4-Pyridyl	C_6H_5	270 (4.39)	
XVIIIf	4-Pyridyl	4-$HOOCC_6H_4$	280 (4.46)	10

(a) Reference 15.

sulfonylhydrazones (VII-XI) and diazonium salts, the sequence shown in Scheme 2 is proposed. It is suggested that the first step involves the substitution of the methine hydrogen of the hydrazone to form the formazan (XXI) (12). The fact that the yield of the tetrazoles is higher in pyridine than in sodium hydroxide- or sodium acetate-ethanol solution is probably attributed to the lower solubility of the hydrazones in the cold alkaline ethanol-water system. In addition, the low yield of the tetrazole (XIVc) in the case of 4-methoxybenzaldehyde hydrazone (VII, Ar^1 = 4-methoxyphenyl) can be accounted for by the autogenistic resonance effect of the 4-methoxyphenyl group on the azocarbanion structure of the hydrazonide anion.

Three alternative routes can account for the conversion of the formazan intermediate (XXI) into the tetrazoles prepared (Scheme 2). Of these three sequences, the first sequence A seems to be the most probable. In sequence A, the ease of elimination of the benzenesulfinate ion is facilitated by the increased delocalization of the π-electrons and the participation of a lone pair orbital of nitrogen in the transition state. On the other hand, in sequence C, the tetrazolinide ion (XXIV) lacks the aromatic stabilization. The sequence B is similar to the Bamford type in the pyrazole synthesis from α,β-unsaturated aldehyde tosylhydrazones (13), by α-elimination of benzenesulfinic acid. However, it seems not operating, as in the present tetrazole formation, the elimination of benzenesulfinic acid occurs much more readily as compared with that in the Bamford reaction (14).

The concerted sequence A is also favoured by the analogy of the proposed transition state (XXII) with the pentadienyl anion. Both the latter ion and the formazanide ion (XXII) are isoelectronic and their most favoured configuration would therefore be the planar U-shaped form. The U-shaped form was reported (15) to possess some quasi-aromatic character. In this configuration, the formazanide ion might pass into the transition state, in which a three centre-four orbital interaction arises between 1-N, 5-N and the phenylsulfonyl group with a more stabilized 6π-electron structure.

Table IV

Acid Dissociation Constant of the Tetrazoles (XIVa-f)

Compound	p*Ka*
XIVa	5.52
XIVb	6.13
XIVc	5.67
XIVd	6.10
XIVe	6.12
XIVf	6.30
Benzoic acid	6.45

EXPERIMENTAL

Melting points are uncorrected. Microanalyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, B.R.D. Part of the analyses was made at the Microanalytical unit, Cairo University, A.R.E. The infrared and electronic spectra were measured on Unicam SP-1000 and Unicam SP-8000 spectrophotometers, respectively.

Aldehyde Phenylsulfonylhydrazones - General Procedure.

To a boiling solution of phenylsulfonylhydrazine (16) (5.1 g., 0.03 mole) in ethanol (50 ml.) acidified with few drops of hydrochloric acid (1*N*), was added dropwise, a solution of the aldehyde (0.03 mole) in ethanol (15 ml.). After complete addition (15 minutes), the reaction mixture was cooled where the hydrazone was separated in a crystalline form. The product was

filtered, washed several times with water, and crystallized from ethanol. The hydrazones were obtained in 40-80% yield, of which the newly prepared ones are listed in Table I along with their analytical data.

Pyridine-4-aldehyde Phenylsulfonylhydrazone (XI).

Phenylsulfonylhydrazine (5.1 g., 0.03 mole) was dissolved in hot methanol (20 ml.) and then left to cool to about 45°. To the resulting cold solution, pyridine-4-aldehyde (3.2 g., 0.03 mole) in methanol (10 ml.) was added dropwise and the reaction mixture was cooled. The precipitated hydrazone was filtered, washed with water, and crystallized from a chloroform-benzene mixture (*cf.*, Table I). Because of the decomposition of this hydrazone on standing, it was used directly after crystallization.

2,5-Disubstituted Tetrazoles (XIV-XIX) - General Procedure.

The appropriate amine (0.01 mole) was dissolved in concentrated hydrochloric acid (3.2 ml.) and an equal volume of water; then cooled to 0°. To the amine hydrochloride solution, was added concentrated solution of sodium nitrite (0.7 g. in 5 ml. water) at 0°, and the mixture was left at 0° for 15 minutes. The diazonium salt solution was then added dropwise to a cold solution of the hydrazone (0.01 mole) in pyridine (20 ml.) where the colour darkened after every addition of the diazonium solution then returned to the original colour again. After complete addition, the reaction mixture was left overnight in a refrigerator. The precipitate was filtered, washed several times with water, and then crystallized from a suitable solvent. Table II lists the tetrazoles prepared together with their physical constants, analytical, and spectral data.

Repitition of the reaction between the diazotized arylamines and aldehyde phenylsulfonylhydrazones in an ethanol-sodium acetate buffered solution gave the corresponding tetrazoles in less than 15% yield.

Determination of the p*K*a of the Tetrazoles (XIVa-f).

A Radiometer *p*H meter model 63 (accurate to ± 0.01 *p*H unit) equipped with combined glass electrode type (GK 2301 C) was used for *p*H titration. The *p*H meter was standardized before use with Radiometer buffers of *p*H 4.00, 7.00 and 9.1. Solutions of the tetrazoles (10^{-3} *M*) in a 50% volume methoxyethanol-water mixture were titrated with standard carbonate-free sodium hydroxide solution (0.102 F) delivered from calibrated automatic burette type Metrohm Herisau Dosimat E415, accurate to ± 0.005 ml. In each titration the initial volume of the solution was 25 ml. The measurements were done at μ = 0.1 *M* potassium nitrate and 25° in a tightly covered thermostated 50 ml. titration cell. The solution was mechanically stirred. A complete titration consisted of successive additions of 0.01-0.02 ml. of the titrant. One half minute after each addition, the stirring motor was stopped and the *p*H-meter reading was taken. The titration was continued until the *p*H-meter could not be kept steady. The dissociation constants were calculated according to the method of Gustafson and Martell (17).

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