[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

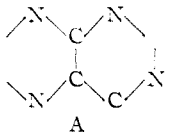
Studies in Imidazoles. I. Imidazo(b)quinoxalines[1,2]

BY EDGAR SCHIPPER[3] AND ALLAN R. DAY

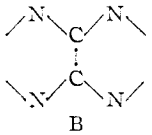
The synthesis of imidazo(b)quinoxalines was undertaken in the hope that these compounds would act as antagonists to certain structurally related essential metabolites. The imidazo(b)quinoxaline ring system was prepared by the interaction of 2,3-diaminoquinoxalines with aldehydes, acyl halides, acid anhydrides, formic acid, orthoesters and urea. In contrast to most other fused ring imidazoles, the imidazole moiety in imidazo(b)quinoxalines is easily hydrolyzed in the presence of acid or base.

In recent years numerous examples of growth inhibitors of microörganisms by chemical analogs of essential nutrilites have appeared in the literature.[4]

The configuration (A) is incorporated in the ring systems of a number of substances which are indispensable for normal metabolic functions. Thus this grouping is found in the isoalloxazine ring of riboflavin, in the pterin structure of folic acid and in purines.

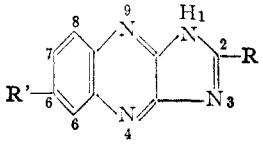


A



B

The configuration (B) containing the oxamidine structure is not found in nature and has received little attention in chemical investigations. The present work was prompted by the idea that the oxamidine configuration, as a part of an appropriate ring system, may provide by its close structural relationship to configuration (A) a suitable competitor for the latter in biological systems. One of the ring systems selected for this study was imidazo(b)quinoxaline (I) whose preparation and characterization is described in this paper.



R = H, alkyl or aryl
R' = H, CH_3 or Cl

I

Of the imidazo(b)quinoxalines only a few possessing a 2-aryl substituent had been reported previously.[5] These compounds had been prepared by condensing equimolecular quantities of 2,3-diaminoquinoxaline with aromatic aldehydes.

The 2-phenyl and 2-β-phenylvinyl derivatives were prepared during the present investigation from benzaldehyde and cinnamaldehyde, respectively. This method failed with aliphatic aldehydes which had reactive α-hydrogen atoms, as only self-condensation or polymerization of the aldehydes occurred under the conditions used. However, with 2-ethylhexanal and 2-ethylbutanal (aldehydes with relatively inert α-positions) the desired reaction took place and the corresponding 2-(1-ethylpentyl)- and 2-(1-ethylpropyl)-imidazo(b)quinoxalines were formed.

The Phillips procedure[6] for the preparation of benzimidazoles from *o*-phenylene diamines cannot be applied to 2,3-diaminoquinoxaline since the latter is rapidly hydrolyzed by mineral acids to 2-hydroxy-3-aminoquinoxaline.[7]

With the exception of formic acid, organic acids did not react with 2,3-diaminoquinoxaline to form imidazo(b)quinoxalines. Reaction of the diamine with formic acid gave the unsubstituted imidazo(b)quinoxaline in rather poor yield.

Ortho esters, in a few cases, have been used to effect intramolecular amidine formation with diamines.[8] No investigation of the reaction of ortho esters with *o*-diamines has been reported. It was found that when 2,3-diaminoquinoxaline was heated with ethyl orthoformate an excellent yield of imidazo(b)quinoxaline was obtained. When ethyl orthoacetate was used, 2-methylimidazo(b)quinoxaline was obtained but in lower yields.

A more general method for preparing 2-alkyl-substituted imidazo(b)quinoxalines was developed using acyl chlorides or anhydrides as acylating reagents in pyridine or xylene as the solvent. The yields decreased as the chain length of the acylating agent increased. Aromatic acyl chlorides failed to give any of the desired imidazoles; however, furoyl chloride gave a low yield of 2-(2'-furyl)-imidazo(b)quinoxaline. With succinic anhydride the expected 2-β-imidazo(b)quinoxaline propionic acid was obtained—a reaction which finds an analogy in the benzimidazole series.[9] The acid chlorides of dibasic acids (such as succinic and adipic) reacted vigorously with the diaminoquinoxaline to give unidentifiable tars instead of the expected bis-imidazoles. Oxalyl chloride, however, gave 2-hydroxyimidazo(b)quinoxaline, identical with that obtained from the fusion of 2,3-diaminoquinoxaline with urea. It is interesting to note that fusion of the thiourea, in contrast to the benzimidazole series,[10] did not produce the corresponding thiol derivative.

To achieve a closer structural relationship to the isoalloxazine structure of riboflavin, two compounds (II, III) were prepared in the imidazo(b)quinoxaline series in which the quinoxaline nitrogen was substi-

(1) From a thesis submitted in February, 1951, by E. Schipper to the Department of Chemistry and Chemical Engineering of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented in part at the 118th Meeting of the American Chemical Society in Chicago, September 8, 1950.

(3) National Institute of Health Predoctoral Research Fellow 1949-1950.

(4) R. O. Roblin, *Chem. Revs.*, **38**, 255 (1946); D. W. Wooley, *Physiol. Revs.*, **27**, 308 (1947).

(5) A. C. Sircar and I. B. Pal, *J. Ind. Chem. Soc.*, **9**, 527 (1932).

(6) M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

(7) J. A. Bladin, *Ber.*, **18**, 666 (1885).

(8) T. Curtius and K. Heidenreich, *ibid.*, **27**, 2684 (1894); R. V. Walther and R. Bamberg, *J. prakt. Chem.*, **68**, 464 (1906); E. C. Wagner, *J. Org. Chem.*, **5**, 133 (1940); A. H. Cook and E. Smith, *J. Chem. Soc.*, 2329 (1949).

(9) B. Chatterjee, *ibid.*, 2965 (1929).

(10) O. Kym, *J. prakt. Chem.*, **75**, 323 (1907).

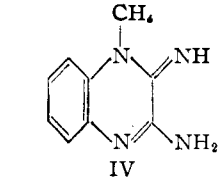
TABLE I

IMIDAZO(b)QUINOXALINES

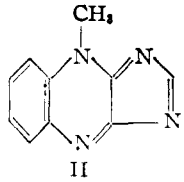
R	R'	Yield, %	Reagent used for ring closure	M.p., °C.[a]	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen (Dumas) Calcd.	Nitrogen (Dumas) Found
H	H	41	HCOOH	286	63.52	63.60	3.55	3.63	32.93	32.96
		86	$HC(OCH_3)_3$							
CH_3	H	30	$CH_3C(OC_2H_5)_3$	322	65.20	65.41	4.38	4.50	30.43	30.43
		86	CH_3COCl							
		96	$(CH_3CO)_2O$							
C_2H_5	H	77	RCOCl	313	66.65	66.77	5.09	5.14	28.26	28.32
		61	$(RCO)_2O$							
n-C_3H_7	H	68	RCOCl	286	67.90	68.21	5.70	5.63	26.40	26.52
n-C_4H_9	H	60	RCOCl	250	69.00	68.93	6.24	6.07	24.76	24.87
n-C_6H_{11}	H	47	RCOCl	242	69.97	70.07	6.71	6.56	23.32	23.15
$(C_2H_5)_2CH$	H	37	RCOCl	246	69.97	70.00	6.71	6.58	23.32	23.43
$(CH_3)_2CHCH_2CH_2$	H	43	RCOCl	223	69.97	70.18	6.71	6.59	23.32	23.45
$C_4H_9CH(C_2H_5)$	H	42	RCHO	221	71.61	71.52	7.51	7.28	20.88	20.69
CH_3OCH_2	H	56	RCOCl	233	61.66	61.55	4.71	4.90	26.16	26.00
$C_6H_{11}CH_2$	H	60	RCOCl	324	72.15	72.25	6.81	6.63	21.04	21.09
$C_6H_5CH_2$	H	52	RCOCl	276	73.81	74.07	4.56	4.53	21.54	21.71
$C_6H_5CH{=}CH$	H	32	ArCHO	311	74.97	74.76	4.45	4.31	20.58	20.70
		65	ArCOCl							
C_6H_5	H	58	ArCHO	324[b]	73.17	73.26	4.07	3.98	22.76	22.63
$HOOCCH_2CH_2$	H	87	$(RCO)_2O$	284	59.50	59.53	4.16	4.25	23.13	23.27
OH	H	65	$(COCl)_2$	447	58.07	58.13	3.22	3.31	30.11	30.28
		86	Urea							
H	CH_3	74	$HC(OCH_3)_3$	246	65.20	65.13	4.38	4.53	30.43	30.40
CH_3	CH_3	84	$(CH_3CO)_2O$	305	66.65	66.54	5.09	5.26	28.26	28.11
C_2H_5	CH_3	67	RCOCl	273	67.90	68.24	5.70	5.83	26.40	26.55
n-C_3H_7	CH_3	88	RCOCl	271	69.00	69.19	6.24	6.31	24.76	24.71
i-C_3H_7	CH_3	54	RCOCl	250	69.00	69.31	6.24	6.20	24.76	24.95
n-C_6H_{11}	CH_3	55	RCOCl	224	70.80	71.07	7.13	7.20	22.07	21.92
$(C_2H_5)_2CH$	CH_3	52	RCOCl	247	70.80	70.70	7.13	7.11	22.07	21.93
$HOOCCH_2CH_2$	CH_3	65	$(CH_3CO)_2O$	283	60.92	60.98	4.74	4.68	21.87	21.40
OH	CH_3	96	Urea	400	59.99	59.93	4.03	4.18	27.99	28.18
CH_3	Cl	77	$(CH_3CO)_2O$	344	54.92	55.11	3.23	3.13	25.63	25.69
OH	Cl	65	Urea	362	48.99	49.06	2.26	2.17	25.40	25.56

[a] All. m.p.'s corrected. [b] Sircar and Pal reported 290°, ref. 5.

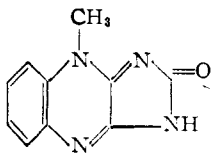
tuted. The synthesis of these isoimidazo(b)quinoxalines was accomplished by heating 1-methyl-2-imino-3-amino-1,2-dihydroquinoxaline (IV) with ethyl orthoformate and urea, respectively.



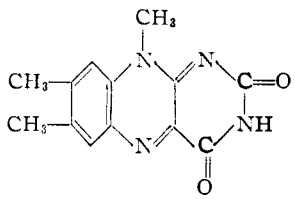
IV



II



III



lumiriboflavin

The types of imidazoquinoxalines synthesized in this study and the method of preparation are listed in Table I.

Physical and Chemical Properties.—With the exception of the 2-aryl derivatives, the imidazo(b)-quinoxalines are colorless compounds. Dilute acetic acid is the best recrystallizing medium for the imidazo(b)quinoxalines. Insoluble hydrochlorides and picrates may be precipitated from alcohol solutions. With aqueous sodium hydroxide salts are formed which are not too soluble in cold water and hence can be recrystallized from this medium. Replacement of the hydrogen atom in position two with a methyl group produces an appreciable decrease in acidity. Increasing the bulk of the 2-alkyl substituent does not produce corresponding decreases in acidity. The following pK_a values are for 50% ethanol solutions: imidazo(b)quinoxaline 9.5; 2-methylimidazo(b)quinoxaline 9.9; 2-n-butylimidazo(b)quinoxaline 10.1; 2-(3'-methylbutyl)-imidazo(b)quinoxaline 10.0. The high melting points of the imidazo(b)quinoxalines indicate that they are strongly associated. This is confirmed by the fact that the nitrogen substituted imidazo(b)-quinoxalines have markedly lower melting points.

The imidazole ring in the imidazoquinoxaline is very susceptible to hydrolysis. With hot dilute hydrochloric the hydrolysis proceeds very rapidly to 2-hydroxy-3-aminoquinoxaline. With dilute sodium hydroxide solution, hydrolysis becomes appreciable after one hour of refluxing, 2,3-diaminoquinoxaline being formed. In view of this ease of hydrolysis it was surprising to find that imidazo(b) quinoxaline was not attacked by benzoyl chloride

under the conditions of the Schotten–Baumann reaction. The latter reaction proceeds readily in the benzimidazole and imidazole series causing the cleavage of the imidazole ring.

Theoretically the imidazo(b)quinoxalines are capable of existing in two tautomeric forms (in addition to the tautomerism within the imidazole ring) which may be designated as "normal" and "iso" forms. No evidence could be obtained for the iso

normal iso

form. Acetylation of 2,3-diaminoquinoxaline with excess acetic anhydride gave the same N-acetyl-2-methylimidazo(b)quinoxaline as that obtained by the direct acetylation of 2-methylimidazo(b)quinoxaline. Since only one N-acetyl derivative is formed it seems probable that imidazo(b)quinoxaline reacts in only one of the two forms. That the reactive tautomer is best represented by the normal structure is indicated from a comparison of the physical properties of imidazo(b)quinoxaline (I), N-acetyl-2-methylimidazo(b)quinoxaline (V) and 4-methyl isoimidazo(b)quinoxaline (II). Both (I) and (V) are colorless, stable compounds. However, (II) darkens perceptibly on standing in air and light, melts with vigorous decomposition and most important of all is a colored compound.

No differentiation between the normal and iso structures was possible on the basis of the spectra of (I) and (V) in the ultraviolet region (Fig. 1). This is not surprising, however, since it has been shown that alloxazine and riboflavin (with its isoalloxazine structure) exhibit similar absorptions.[11] The ultraviolet absorption of the imidazo(b)quinoxalines, as

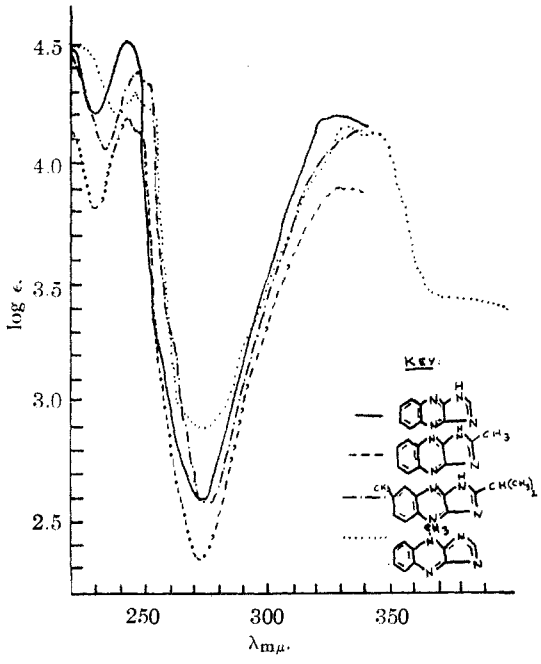


Fig. 1.

(11) R. Kuhn and F. Bar, *Ber.*, **67**, 898 (1934).

a group, resembles that of quinoxaline.[11] The observation that the imidazole unit apparently contributes little to the ultraviolet spectrum is in agreement with the findings of Cavalieri and co-workers on the spectra of purines.[12]

Imidazo(b)quinoxalines are not attacked by potassium permanganate at room temperature. Thus the double bond in the side chain of 2-β-phenylvinylimidazo(b)quinoxaline can be oxidized to give imidazo(b)quinoxaline, the intermediate acid apparently undergoing spontaneous decarboxylation.

Similar to many other aromatic nitrogen bases including benzimidazoles, the methyl group in 2-methylimidazo(b)quinoxaline possesses considerable active methylene character. When this compound is refluxed with benzaldehyde in the presence of piperidine, 2-β-phenylvinylimidazo(b)quinoxaline is formed.

Experimental

2,3-Diaminoquinoxaline.—This compound was prepared by the procedure of Hinsberg and Schwantes.[13] It was noted that the presence of a few drops of water was necessary for the reaction to take place. Better yields were obtained when 1 cc. of 10% sodium hydroxide was added for each 100 cc. of methanol used; yield 48%, m.p. 331°.

2,3-Diamino-6-methylquinoxaline.—The above procedure was applied to 1,2-diamino-4-methylbenzene; yield 40%, m.p. 249° (Bladin[7] reported m.p. 242–244°).

2,3-Diamino-6-chloroquinoxaline.—In this case the modified Hinsberg–Schwantes procedure was applied to 1,2-diamino-4-chlorobenzene; yield 35%, m.p. 286°. A sample was prepared for analysis by recrystallization from pyridine followed by sublimation at 200° and 1 mm.

Anal. Calcd. for $C_8H_7N_4Cl$: C, 49.36; H, 3.63; N, 28.80. Found: C, 49.45; H, 3.67; N, 29.08.

1-Methyl-2-imino-3-amino-1,2-dihydroquinoxaline.—The above procedure was applied to N-methyl-*o*-phenylenediamine; yield 26%, m.p. 203–204°. A sample was sublimed at 150° for analysis.

Anal. Calcd. for $C_9H_{10}N_4$: C, 62.05; H, 5.78; N, 32.17. Found: C, 61.90; H, 5.85; N, 32.21.

Imidazo(b)quinoxalines. Reaction of the Diamine with Aldehydes.—Two grams of 2,3-diaminoquinoxaline, 1.4 g. of benzaldehyde, 25 ml. of pyridine, 1.5 ml. of 40% sodium hydroxide and 75 ml. of ammonium hydroxide were refluxed for 3 hours.[14] The solvent was removed under reduced pressure and the residue dissolved in boiling 1 *N* sodium hydroxide. The hot solution was filtered and the filtrate neutralized with acetic acid. The crude product was recrystallized from dilute acetic acid. The same procedure was used for the preparation of 2-β-phenylvinylimidazo(b)quinoxaline.

This method cannot be used with aliphatic aldehydes which have active methylene groups because of the tendency for the occurrence of self-addition. The procedure, however, gives good results with 2-substituted aldehydes. However, it had to be modified in order to obtain the desired product. Two grams of 2,3-diaminoquinoxaline, 2 g. of 2-ethylhexanal, 3 ml. of aqueous Triton B (40%) and 25 ml. of pyridine were allowed to stand at room temperature for five days. The product which separated during that time was recrystallized from dilute acetic acid using Darco as the decolorizing agent.

Reaction of the Diamine with Formic Acid.—2,3-Diaminoquinoxaline was heated for 4 hours, just below the refluxing temperature, with ten equivalents of pure formic acid. The excess formic acid was removed under reduced pressure, the residue extracted with boiling 10% sodium hydroxide, filtered and the filtrate neutralized with acetic acid. The crude product so obtained was recrystallized from dilute acetic using Darco as the decolorizing agent.

(12) L. F. Cavalieri, A. Bendich, F. Tinker and G. B. Brown, THIS JOURNAL, **70**, 3875 (1948).

(13) O. Hinsberg and E. Schwantes, *Ber.*, **36**, 4039 (1903).

(14) Sircar and Pal[5] did not use a base catalyst in their procedure.

Reaction of the Diamine with Orthoesters.—2,3-Diaminoquinoxaline was suspended in five equivalents of ethyl orthoformate. The mixture was heated in an oil-bath maintained at 140–145° for six hours, with stirring. At this temperature a slow distillation of ethyl orthoformate took place. The volume was kept constant by a dropwise addition of fresh orthoformate. At the end of the reaction period the excess of ethyl orthoformate was removed under reduced pressure and the residue worked up in the manner described above for the formic acid method.

2-Methylimidazo(b)quinoxaline was prepared in a similar way using ethyl orthoacetate in place of ethyl orthoformate.

Reaction of the Diamine with Acyl Halides.—The following example illustrates the general method. Three grams of acetyl chloride was added to 25 ml. of cold pyridine. Then 5 g. of 2,3-diaminoquinoxaline was added with stirring and the mixture slowly heated on a steam-bath until most of the solid had gone into solution. The reaction mixture was heated at 100° for three hours and the excess solvent then removed under reduced pressure. The residues were worked up according to the directions given under "Reaction of the Diamine with Formic Acid."

Minor modifications were made in the above method for certain acyl halides. Where methoxyacetyl chloride was used, a trace of concentrated sulfuric acid was added to the reaction mixture. With phenylacetyl and furoyl chlorides, xylene proved to be a better solvent than pyridine.

With aromatic acyl chlorides, products were obtained which were consistently high in carbon. This problem has not been resolved successfully up to now.

Reaction of the Diamine with Acid Anhydrides.—2,3-Diaminoquinoxaline was refluxed for one hour with six equivalents of acetic anhydride. Crude 1-acetyl-2-methylimidazo(b)quinoxaline separated on standing overnight. It was recrystallized from dry ethanol using Darco as the decolorizing agent; yield 72%, m.p. 158–159°.

Anal. Calcd. for $C_{11}H_8ON_4$: C, 63.70; H, 4.45; N, 24.77. Found: C, 63.54; H, 4.28; N, 24.88.

The 1-acetyl derivative is converted to 2-methylimidazo(b)quinoxaline by boiling for a few minutes with dilute sodium hydroxide solution.

The reaction of the diamine with succinic anhydride was carried out in pyridine solution as described for the acyl chlorides. The crude 2-β-imidazo(b)quinoxaline propionic acid so obtained was recrystallized from 70% ethanol.

Fusion of the Diamine with Urea.—A mixture of 2,3-diaminoquinoxaline with two moles of urea was heated at 180° until no more ammonia evolved. The residue was broken up and washed with alcohol. The product was then dissolved in hot concentrated ammonium hydroxide, decolorized with Darco and filtered. Neutralization of the filtrate with acetic acid precipitated the imidazolone.

Preparation of 4-Methylisoimidazoquinoxaline.—1-Methyl-2-imino-3-amino-1,2-dihydroquinoxaline was heated with ethyl orthoformate as previously described for 2,3-diaminoquinoxaline. After removal of the ethyl orthoformate, the residue was dissolved in a minimum amount of butanol-2, decolorized with Darco and filtered. The filtrate was diluted with an equal volume of dry ether and kept at 0° for 24 hours; yield 66%, m.p. 210–213° dec.

Anal. Calcd. for $C_{10}H_8O_4$: C, 65.20; H, 4.38; N, 30.43. Found: C, 65.33; H, 4.09; N, 30.20.

Preparation of 2-Hydroxy-4-methylisoimidazoquinoxaline.—1-Methyl-2-imino-3-amino-1,2-dihydroquinoxaline was fused with urea by the procedure previously described. The fusion temperature was 150–155°; yield 61%, m.p. 355°.

Anal. Calcd. for $C_{10}H_8ON_4$: C, 59.99; H, 4.03; N, 27.99. Found: C, 60.06; H, 4.16; N, 27.74.

Hydrolysis of Imidazo(b)quinoxaline. Acid Hydrolysis.—One gram of imidazo(b)quinoxaline was refluxed for five minutes with 20 ml. of 2.5 *N* hydrochloric acid. Neutralization of the solution with ammonium hydroxide precipitated an almost quantitative yield of 2-hydroxy-3-aminoquinoxaline. It proved to be identical with an authentic sample.[15]

Anal. Calcd. for $C_8H_7ON_3$: C, 59.58; H, 4.37; N, 26.08. Found: C, 59.69; H, 4.26; N, 25.99.

Basic Hydrolysis.—One gram of imidazo(b)quinoxaline was refluxed for one hour with 100 ml. of 1 *N* sodium hydroxide. After cooling a 65% yield of 2,3-diaminoquinoxaline was obtained.

Oxidation of 2-β-Phenylvinylimidazo(b)quinoxaline.—Two grams of 2-β-phenylvinylimidazo(b)quinoxaline was dissolved in 200 ml. of pyridine. With stirring, 612 ml. of 0.5% potassium permanganate was added gradually with stirring. The mixture was allowed to stand overnight and filtered. The filtrate was heated to boiling and again filtered. Neutralization of the filtrate with acetic acid precipitated imidazo(b)quinoxaline, yield 35%.

Condensation of 2-Methylimidazo(b)quinoxaline with Benzaldehyde.—One gram of 2-methylimidazo(b)quinoxaline was refluxed with 5 ml. of benzaldehyde and 0.5 ml. of piperidine for two hours. The product obtained on cooling was washed with ether, then dissolved in hot dilute sodium hydroxide and reprecipitated by neutralizing with acetic acid; yield of 2-β-phenylvinylimidazo(b)quinoxaline, 83%.

(15) J. R. Stevens, K. Pfister and J. Wolf, THIS JOURNAL, **68**, 1035 (1946).

PHILADELPHIA, PENNA. RECEIVED MARCH 28, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions of N-Monoalkylhydroxylamines with Sulfur Dioxide, Sulfur Trioxide and Phthalic Anhydride [1]

BY AUGUST I. RYER[2] AND G. B. L. SMITH[3]

The crystalline N-monoalkylhydroxylamines (hydroxaminoalkanes), N-isopropylhydroxylamine (2-hydroxaminopropane), N-(*n*-propyl)-hydroxylamine (1-hydroxaminopropane) and N-ethylhydroxylamine (hydroxaminoethane) have been isolated in crystalline form and the oxalates of the first two have been prepared. These alkylhydroxylamines yield alkylsulfamic acids with sulfur dioxide and N-alkylhydroxaminosulfonic acids (N-alkyl-N-hydroxysulfamic acids) with sulfur trioxide. The N-monoalkylhydroxylamines with phthalic anhydride give N-alkyl-N-hydroxyphthalamic anhydrides rather than the N-alkyl-N-hydroxyphthalamic acids although the copper salts of the latter were isolated as dihydrates.

Introduction

Although N-monoalkylhydroxylamines have been known for over 50 years, few reactions of these compounds have been studied. Early investigators[4] prepared the N-monoalkylhydroxylamines by the reduction of the corresponding nitroparaffins.

The electrochemical reduction of the commercial nitroparaffins was studied by Leeds and Smith[5] who developed a simple process for the preparation of the N-alkylhydroxylamines. They did not,

(1) From the doctoral dissertation of August I. Ryer submitted to the Faculty of the Graduate School of Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in June, 1946.

(2) Schering Corporation, Bloomfield, New Jersey.

(3) Chemistry Division, U. S. Naval Ordnance Test Station, Inyokern, Post Office, China Lake, California.

(4) E. Hoffman and Victor Meyer, *Ber.*, **24**, 3528 (1891); A. Kirpal, *ibid.*, **25**, 1714 (1892); E. Bamberger, *ibid.*, **27**, 1347 (1894); P. Pierron, *Bull. soc. chim.*, **21**, 780 (1899).

(5) M. W. Leeds and G. B. L. Smith, *J. Electrochem. Soc.*, **98**, 129 (1951).