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N-OXIDES IN THE QUINOXALINE SERIES

IX. Tautomerism of 2-Acetylaminoquinoxalines and Their N-Oxides*

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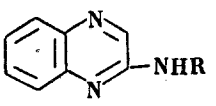
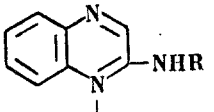
Acyl derivatives of 2-aminoquinoxaline and their 1-N-oxides, as well as methyl derivatives of some of those compounds, are synthesized. IR spectra of these compounds in the solid state, and UV spectra of their solutions, showed that, with respect to the ability of its 2-acylamino derivatives to tautomerize to the imido form, quinoxaline is close to pyrimidine, and below quinoline and pyridine. With respect to the amide-imide tautomerism equilibrium position, N-oxides of 2-acylaminoquinoxalines differ little from acylamides of quinoxaline themselves. The action of benzene sulfochloride on 2-aminoquinoxaline-1-N-oxide in pyridine below 0°leads to deoxidation of the N → O group, and introduction of the benzene sulfonyloxy group at position 3 in the quinoxaline ring.

A previous paper in this series described the synthesis of mono- and di-N-oxides of 2-aminoquinoxaline and its acetyl derivatives [1]. By analogy with α- and γ-amines of other 6-membered ring aromatic azines and their N-oxides [2-5], 2-aminoquinoxaline (I) and its 1-N-oxide (II) must exist in the amino form both in the crystalline state, and in solution. It was previously shown [6] that substitution of the hydrogen of the amino groups with electronegative substituents (e.g., by acid groups), can, by decreasing the basicity of the extra-nuclear nitrogen atom, shift the tautomeric equilibrium of α- and γ-amino derivatives of N-heterocyclic compounds over to the side where the imino form predominates. With one and the same "acid" group in different heterocyclic systems, the degree of shift of amino form towards imino form depends on the ratio of the dissociation constants of amino and imino forms, and that is, in particular, conditioned by the nature of the heterocyclic ring system. From that point of view it was of interest to investigate the acylated derivatives I and to compare them with the corresponding derivatives of compound II. We have also synthesized the following acyl derivatives of general formulas III and IV.



III



IV

a R=COC_6H_5; b R=$COOCH_3$; c R=$COCHCl_2$; d R=$COCCl_3$; e R=$COCF_3$; f R=$SO_2C_6H_5$.

All the compounds mentioned above, with the exception of IVf, were prepared by treating I or II with the acid chlorides or anhydrides of the appropriate acids, while with IIIb and IVb, methyl chloroformate was used. Compound IVf was prepared by reacting benzenesulfonamide with 2-chloroquinoxaline-1-N-oxide, which latter was previously synthesized [7]. In an attempt to prepare compound IVf by acylating compound II with benzenesulfochloride in the presence of pyridine, the main reaction product isolated was 2-amino-3-benzenesulfonyloxyquinoxaline. The structure of this compound is proved by the elementary analytical data, and its IR spectrum having bands in the regions 3500, 3215, 3130 cm^{-1}, connected with valence vibrations of the group NH_2, and a band at 1655 cm^{-1} due to deformation vibrations of the same group, and by its acid hydrolysis to 2-amino-3-hydroxyquinoxaline.

For comparison of the spectra of the acylamino derivatives prepared with those of models, of the so called "locked" tautomeric forms, the following methyl derivatives were synthesized by methylating the corresponding acylamines with dimethyl sulfate in alkali: 2-N-acetylmethylaminoquinoxaline (V) (the IR spectrum has an amide carbonyl band at 1680 cm^{-1}), 1-methyl-2-trichloroacetylimino-1, 2-dihydroquinoxaline (VI), and 1-methoxy-2-trichloroacetylimino-1, 2-dihydroquinoxaline (VII). A conclusion regarding the structures of VI and VII was reached, starting from the fact that the C=O bands in the IR spectra of these compounds were displaced towards the lower frequencies (1646 and 1660 cm^{-1} respectively), which indicated conjugation of the carbonyl group with the C=N double bond, characteristic of the imide structure (C=N−C=O). Had compounds VI and VII existed in amide form, the C=O bands in the IR spectra of those compounds should have been considerably shifted towards the higher frequency region (1720-1740 cm^{-1}), on account of the inductive effect of the electronegative chlorine atoms on the acyl groups. Methylation of the sodium

*For Part VIII see [17].

salt of IIIf with methyl iodide gives 2-(N-benzenesulfone)-methylamidoquinoxaline (VIII), and 1-methyl-2-benzenesulfonimido-1, 2-dihydroquinoxaline (IX), whose structures were demonstrated by acid hydrolysis. Compound VIII gave 2-methylaminoquinoxaline, as shown by its existence in the locked amide form, and compound IX gave 2-oxo-1, 2-dihydroquinoxaline and benzenesulfonamide. The structures of these compounds were also confirmed by UV spectrum

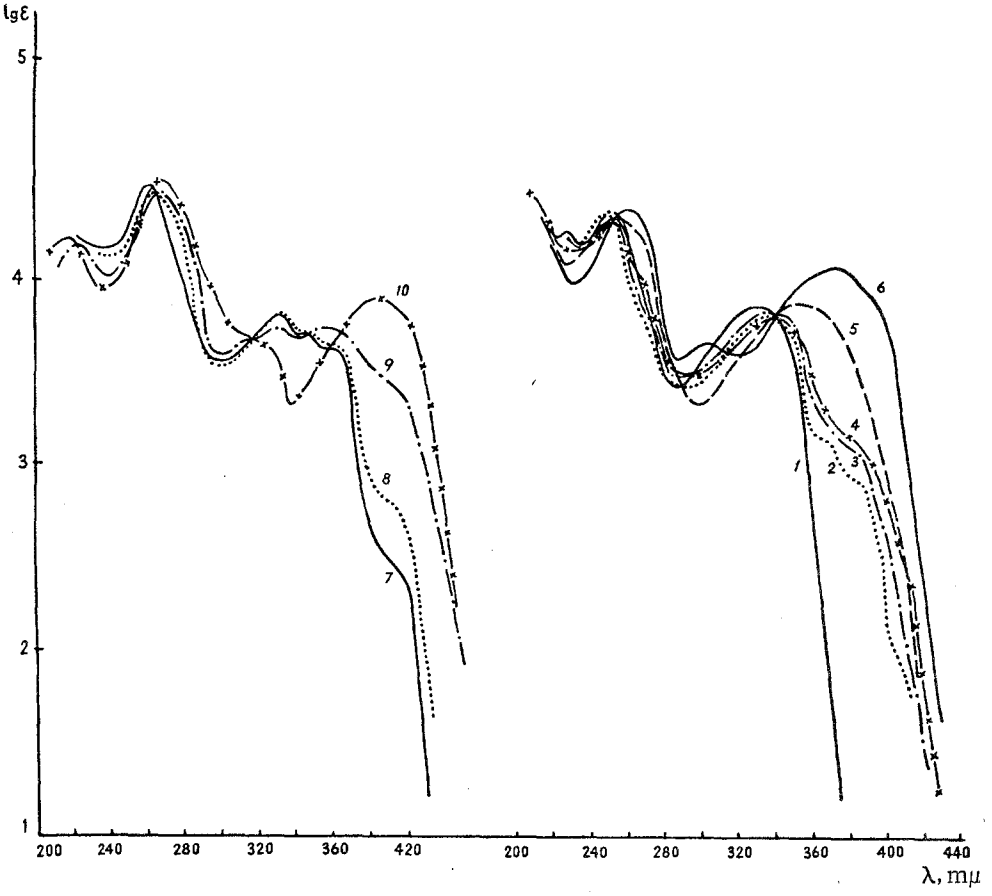


Fig. 1. UV spectra: 1) 2-benzenesulfonemethylamidoquinoxaline (VIII) in dry ethanol; 2-5) 2-benzenesulfonamidoquinoxaline (IIIf) (2 in a mixture of 90% heptane and 10% dioxane; 3 in dioxane; 4 in dry ethanol; 5 in a mixture of 90% water and 10% ethanol); 6) N-methyl-2-benzenesulfonimido-1, 2-dihydroquinoxaline (IX) in dry ethanol. 7-10) 2-Benzenesulfonamidoquinoxaline-1-N-oxide (IVe) (7 in a mixture of 90% heptane and 10% dioxane; 8 in dioxane; 9 in dry ethanol; 10 in a mixture of 90% water and 10% ethanol).

data (Fig. 1). The IR spectra of the compounds investigated were observed with crystals made into a paste with vaseline, with a UR-10 infra-red spectrophotometer. The UV spectra were measured with a SF-4 spectrophotometer, solvents being n-hexane, dioxane, dry EtOH, and water. Table 1 gives the most essential bands in the IR spectra of 2-aminoquinoxaline, its N-oxide, and its acyl derivatives (except for benzenesulfo derivatives).

Consideration of the bands in the 1750-1640 cm^{-1} region, connected with valence vibrations of the C=O group in the compounds under consideration, and comparison of them with the corresponding bands in the "locked" amido and imido forms V, VI, and VII, lead to the conclusion that all the acylamino derivatives I and II, given in Table 1, exist in the amido form in the crystalline state. The considerable increase in frequencies for the C=O amide bands in compounds IIIb-e, and IVb-e, are explained by the inductive effects of the electronegative atoms of chlorine and fluorine, and of the OMe group. The solution of the problem of the structures of the benzenesulfo derivatives of compounds I and II was more complex. It was previously shown [8-9] that with sulfonamide derivatives of N-heterocyclic rings uncondensed with a benzene ring, bands in the region 940-990 cm^{-1} are characteristic of the imido form, and bands in the region 850-890 cm^{-1} are characteristic of the amido form. With the IR spectra of model compounds VIII and IX, having respectively a "locked" amido and imido structure, no bands which could be ascribed to only one of these compounds could be observed. We previously observed this for benzenesulfonamide derivatives. The 1100-1000 cm^{-1} region was more characteristic. The spectrum of VIII had an intense band at 1045 cm^{-1} in that region, absent from the spectrum of compound IX. In the case of compound IX, in its turn an intense band at 1092 cm^{-1} was characteristic of it, one which was weakly represented in the spectrum of compound VIII. The absence of a band in the 1045 cm^{-1}

region from the spectra of compounds IIIf, IVf, and 2-(4'-aminobenzene) sulfonamidoquinoxaline (XII) [10], and their exhibiting an intense band in the 1092-1095 cm^{-1} region, leads weight to the conclusion that these compounds have an imide structure in the crystalline state.

Table 1

IR Spectra Band Frequencies, cm^{-1}

Compound	3400—3100 (NH)	1750—1640 (C=O)	1660—1640 (NH_2)	1600—1480	1300—1200	900—850
I	3380, 3330, 3165	—	1660	1590, 1575	—	—
2-Acetylaminoquinoxaline	3190 (weak)	1707	—	1578, 1495	1250	885 (weak)
IIIa	3230 (weak)	1670	—	1575, 1492	1270	—
IIIb	3138	1744	—	1594, 1496	1257, 1232	—
IIIc	3255	1735	—	1578, 1498	1235	900 (weak)
IIId	3395	1724	—	1573, 1492	1235	895 (weak)
IIIe	3330	1728	—	1585, 1505	1238	—
V	—	1680	—	1554, 1483	1230	—
VI	—	1646	—	1570, 1503	1224	—
II	3310, 3155	—	1645	1608, 1496	1201	880
2-Aminoquinoxaline-4-N oxide (X)	3392, 3190	—	1624	1591, 1560	1215	887
2-aminoquinoxaline-1,4-di-N-oxide	3268	—	1641	1590	1217	—
2-Acetylaminoquinoxaline-1-N-oxide	3200	1705	—	1580, 1497	1270, 1230	870
IVa	3199	1672	—	1570, 1497	1285	870
IVb	3162	1744	—	1597, 1502	1273	872
IVc	3200	1725	—	1572, 1510	1255, 1229	878
IVd	3225 (weak)	1730	—	1570, 1500	—	879
IVe	3270	1735	—	1578, 1505	—	878
VII	—	1660	—	1575, 1510	1280	850

The spectra of almost all the compounds investigated had intense bands at 1605-1570 and 1510-1480 cm^{-1}, evidently ascribable to valence vibrations of ring double bonds. It has previously been shown for N oxides of pyridine, pyrazine, and other heterocyclic compounds, that the characteristic bands of the N → O group are usually manifest in the 1300-1200 cm^{-1} region. These data were confirmed by comparison of spectra of 2-aminoquinoxaline (I), and its N oxide. Thus the spectra of compounds II, X, and XI had intense bands at 1200, 1215, and 1217 cm^{-1}, respectively, which were absent from the spectrum of I. However, in the cases of the spectra of acyl derivatives of compound II, it was impossible to separate characteristic bands in this region. Furthermore, in the cases of the N oxides of acylaminoquinoxalines enumerated above, rather intense bands were found in the 890-870 cm^{-1} region, absent from the spectra of the corresponding non-oxidized bases, or only weakly manifest. Evidently these bands can be related to N → O bond vibrations; such bands were also found for N oxides derived from pyridine (820-860 cm^{-1}) and pyrimidine (855-872 cm^{-1}) [13].

The UV spectra of compounds VI and IX, model imino forms of acylaminoquinoxalines, were found to exhibit two absorption maxima: λ 262-280 mμ, lg ε 4.28-4.38, and λ 375-382 mμ, lg ε 4.08-4.20. In the cases of the spectra of compounds V and VIII these maxima were displaced towards the short wave region (λ 253-257 mμ, lg ε 4.3; λ 332-336 mμ, lg ε 3.86-3.88), and a third maximum appeared at λ 226-230 mμ, lg ε 4.17-4.27.

In the case of N-oxides of acylaminoquinoxalines, we obtained only one model compound, VII, with an imino structure. As the spectrum of this compound resembles that of unoxidized model imido compounds, VI and IX (λ 280 mμ, lg ε 4.25, and λ 3.78 mμ, lg ε 4.13), it was thought possible to use the spectra of model amide compounds V and VIII for comparison, not only with acylaminoquinoxalines, but also with their N oxides. Review of the UV spectra of 2-acylaminoquinoxalines and their N oxides showed that most of them, even those with strong acidifying groups (trifluoro- and trichloroacetic acids) have spectra like models of amide structure (bands in the region λ 250-260 mμ, lg ε 4.38-4.56 and λ 330-348 mμ, lg ε 3.88-4.08), indicating an amide structure for these acylamines. Here, in the N oxides, the short wave maximum was displaced towards the longer wavelength side by 10-15 mμ, but in the long wave region there appeared a further maximum at λ 355-362 mμ, lg ε 3.8-3.9 (Fig. 2).

It should be mentioned that some acylaminoquinoxalines, and particularly their N oxides decomposed into the starting amines in solution, their instabilities being a linear function of the electronegativity of the acyl group and the solvent polarity. Thus when compound IIId was allowed to stand for some days it was completely converted to compound

I; IVd was still more rapidly hydrolyzed in water, while IVe in solution in alcohols showed the presence of II after a few minutes.

In this connection there were certain difficulties with plotting the UV spectra, and to secure the required results, it was necessary to work as fast as possible, using freshly-prepared solutions. In some cases it was generally impossible to obtain spectra with water–ethanol solutions. The possibility is not excluded that a small amount of imide tautomeric form could be detected in acylaminoquinoxalines and their N oxides, e.g., compounds IIId, IIIe, IVd, IVe, if solutions of them in polar solvents were more stable. The benzenesulfamide derivatives IIIf and IVf were considerably more stable compounds, hydrolyzable only under rather drastic conditions. The UV spectra of these compounds, as well as of compound XII and its 4-acetyl derivative showed, in addition to absorption maxima characteristic of the amide tautomeric form, an absorption at 360-400 mμ, whose intensity increased with increase in solvent polarity. In hexane, dioxane, and ethanol, this absorption (360-400 mμ) appeared as wide shoulders. In water–ethanol (90%-10%) the spectrum changed considerably, approximating to that of the model imide compound IX (Fig. 1). From these results it can be concluded, that the imido form is present in solutions of the sulfonamide derivatives investigated, and that the amount increases with increase in solvent polarity. In water–ethanol mixture, compounds IIIf and IVf practically exist as the imino form.

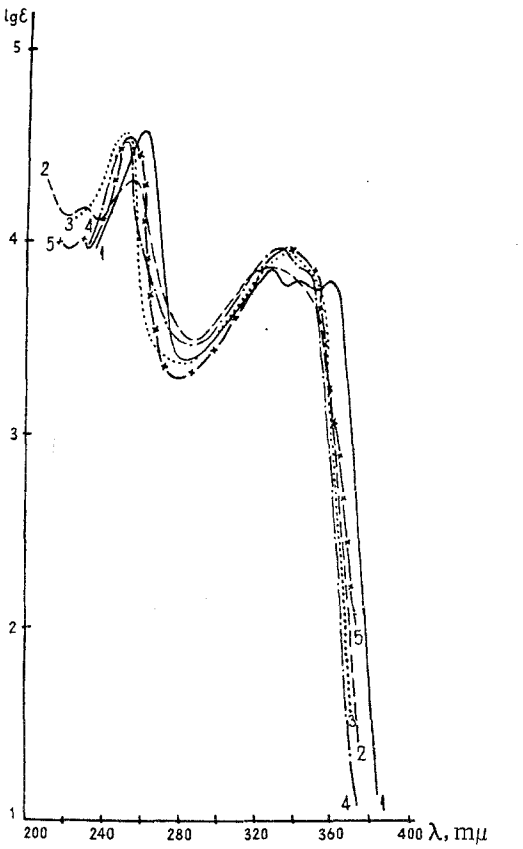


Fig. 2. UV spectra: 1) 2-carbomethoxyaminoquinoxaline-1-N-oxide (IVb) in dioxane; 2) 2-acetylmethylaminoquinoxaline (V) in dry EtOH; 3) 2-carbomethoxyaminoquinoxaline (IIIb) in dry EtOH; 4, 5) 2-acetylaminoquinoxaline (4 in dioxane; 5, in dry EtOH).

Thus review of the IR spectra of crystals and UV spectra of solutions of acyl amines of 2-aminoquinoxaline showed that in respect of a capacity of its 2-acylamino derivatives to go over to an imide form, the quinoxaline ring occupies a position close to that of the pyrimidine ring, i.e., the appropriate change is effected only under the action of the most powerful of the acidifying groups used, benzenesulfono. This agrees with the view that build-up of nitrogen atoms in 6-membered aromatic heterocyclic rings lowers the basicity of cyclic nitrogen atoms [14], and thereby shifts tautomeric equilibrium of the corresponding acylamino derivatives in the direction of higher content of amide form [15]. Such a parallelism is markedly evident on comparing ionization constants (pK_a) of the actual amines (these constants characterizing the capacity of the cyclic nitrogen to hold a proton), with the tendency to shift over to the imido forms of their acyl derivatives. For example, in the series 2-aminoquinoline, 2-aminopyridine, 2-aminopyrimidine, and 2-aminoquinoxaline, the corresponding ionization constants are 7.3, 6.9, 3.5, 3.9, and the capacity of these compounds to go over to the imide tautomeric form lies in the same order. It must be borne in mind that transition from one heterocyclic ring to another changes the basic properties not only of the cyclic but also of the exocyclic nitrogen in the corresponding amines and acylamines. However the comparison effected shows that ring nitrogen hereby suffers greater change of basic properties,

It would be expected, on shifting over to the N-oxides of the corresponding acylamino derivatives, that there would be further weakening of the capacity to go over to the imide form, as it is known that the ionization constant of N oxides in the heterocyclic amine series is considerably less than for the corresponding amines [14, 16]. However, our results show that N oxides of acylaminoquinoxalines are practically the same as quinoxaline acylamides as far as position of the amide-imide tautomeric equilibrium goes. Obviously this can be explained by the strong electron-accepting action of the N → O group on the exocyclic nitrogen atom, lowering its basicity. Because of this the basicity ratio for the amide and imide forms remains practically the same as with the non-oxidized bases.

We thank Prof. O. Yu. Magidson for his interest in our work.

Experimental

2-Benzoylaminoquinoxaline-1-N-oxide (IVa). 0.25 ml (0.0025 mole) benzoyl chloride in 2 ml dry $CHCl_3$ was added to 0.16 g (0.001 mole) 2-aminoquinoxaline-1-N-oxide (II) in 1 ml dry pyridine, the mixture left at 18-20° for 18 hr, then poured into ice water, 2.5 N HCl added to bring the whole to pH 1-2, and the mixture extracted with

$CHCl_3$. Yield 0.13 g IVa, mp 143-144° (ex EtOH). Found: C 67.84; H 4.18; N 15.58%. Calculated for $C_{15}H_{11}N_3O_2$: C 67.93; H 4.18; N 15.84%.

The compounds listed in Table 2 were prepared similarly.

Table 2

Characteristics of Compounds Prepared

Compound number	Mp, °C	Formula	Found, %				Calculated, %			
			C	H	Cl	N	C	H	Cl	N
IVb*	178—179 (ex EtOH)	$C_{10}H_9N_2O_3$	54.66	4.33	—	19.01	54.79	4.14	—	19.17
IVc	159—160 (ex EtOH)	$C_{10}H_7Cl_2N_3O_2$	—	—	26.2	15.55	—	—	26.06	15.44
IVd	145—146 (ex EtOH)	$C_{10}H_6Cl_3N_3O_2$	—	—	34.37	13.84	—	—	34.7	13.71
IVe**	185—186 (ex Et_2O-$CHCl_3$)	$C_{10}H_6F_3N_3O_2$	—	—	F 21.94	—	—	—	F 22.16	—
IIIa	147—148 (ex EtOH)	$C_{15}H_{11}N_3O$	—	—	—	17,2	—	—	—	16.85
IIIb*	188—189 (ex EtOH)	$C_{10}H_9N_3O_2$	58.65	4.40	—	20.49	58.52	4.42	—	20.47
IIIc	135—136 (ex EtOH)	$C_{10}H_7Cl_2N_3O$	47.08	2.77	27.48	16.33	46.89	2.76	27.69	16.41
IIId	107—108 (ex EtOH)	$C_{10}H_6Cl_3N_3O$	—	—	36.97	14.5	—	—	36.61	14.46
IIIe**	155—156 (ex 40% EtOH)	$C_{10}H_6F_3N_3O$	—	—	F 23.62	—	—	—	F 23.63	—
IIIf	176—177 (ex EtOH)	$C_{14}H_{11}N_3O_2S$	—	—	S 10.95	14.72	—	—	S 11.20	14.73
IVf	224—225 (ex EtOH)	$C_{14}H_{11}N_3O_3S$	—	—	S 10.33	14.13	—	—	S 10.64	13.94

* Here the acylating agent was methylchloroformate, reactants held at 35-40°for 3 hr 30 min - 4 hr.

** Trifluoroacetic acid was used instead of the acid chloride.

2-Benzenesulfonamidoquinoxaline-1-N-oxide (IVf). A mixture of 0.45 g (0.0025 mole) 2-chloroquinoxaline-1-N-oxide [7], 0.39 g (0.0025 mole) benzenesulfonamide, and 0.69 g (0.005 mole) anhydrous K_2CO_3 in 10 ml dry EtOH was refluxed for 4 hr, then cooled, the precipitate filtered off, and reprecipitated from 2.5 N NaOH by means of dilute HCl. Yield 0.80 g (IVf) mp 224-225° (ex EtOH). The substance gives an intense violet coloration with aqueous $FeCl_3$.

1-Methyl-2-benzenesulfonimido-1,2-dihydroquinoxaline (IX). A solution of NaOEt, prepared from 0.45 g (0.0195 mole) Na in 30 ml EtOH, was added to 4.26 g (0.0149 mole) IIIf in 15 ml dry EtOH, the Na salt of IIIf formed, filtered off and washed with EtOH. This salt was dissolved in 30 ml 48% EtOH, 2.6 ml MeI in 46 ml 95% EtOH added, the mixture refluxed for 2 hr, cooled, and the IX filtered off. It contained IIIa and VIII as impurities, and was freed from them by alternately washing the precipitate with ether and 2.5 N NaOH. Yield of IX, 1 g, mp 184-185° (ex EtOH). Found: C 60.46; H 4.29; N 14.08; S 10.8%. Calculated for $C_{15}H_{13}N_3O_2S$: C 60.18; H 4.37; N 14.04; S 10.69%.

2-(N-benzenesulfone) methylamidoquinoxaline (VIII). The basically-reacting solution from the previous experiment, after separating off IX, was evaporated to one-third volume under reduced pressure, the residue triturated with 2.5 N NaOH, and the precipitate formed filtered off, yield, 1.45 g VIII, mp 88-89° (ex EtOH-H_2O). Found: N 14.17; S 10.99%. Calculated for $C_{15}H_{13}N_3O_2S$: N 14.04; S 10.69%.

Hydrolysis of 2-(N-benzenesulfone) methylamidoquinoxaline (VIII). 1 g VIII in 10 ml concentrated HCl was heated for 1 hr 30 min, on a boiling water bath, the solution cooled, brought to pH 6 with 2.5 N NaOH, and unreacted VIII (0.2 g) filtered off. The filtrate was brought to pH 8, cooled, and the 2-methylaminoquinoxaline (0.3 g) filtered

off, mp 130-131° (ex H_2O-EtOH). The IR spectrum had a N–H valence vibration band at 3338 cm^{-1}, and bands at 1593 and 1558 cm^{-1}. Found: C 67.69; H 5.73; N 26.00%. Calculated for $C_9H_9N_3$: C 67.90; H 5.70; N 26.39%.

Hydrolysis of 1-methyl-2-benzenesulfonimido-1,2-dihydroquinoxaline (IX). 1 g IX in 4 ml concentrated HCl was heated at the same temperature as above for 3 hr, the solution cooled, and filtered, to give 0.37 g 2-benzenesulfonamide as solid, mp 149-150° (ex water). Found: C 45.76; H 4.66; N 8.94%. Calculated for $C_6H_7NO_2S$: C 45.84; H 4.48; N 8.91%.

After the benzenesulfonamide had been separated off, the reaction solution was brought to pH 5, unreacted IX (0.1 g) separated off, the filtrate made alkaline with excess concentrated NaOH solution, cooled, and the solid 1-methyl-2-oxo-1,2-dihydroquinoxaline (0.25 g) filtered off, mp 118-119° (ex water). The IR spectrum had an amide carbonyl band at 1670 cm^{-1}. Found: C 67.51; H 5.07; N 17.29%. Calculated for $C_9H_8N_2O$: C 67.48; H 5.03; N 17.49%.

2-(Acetylmethylamino) quinoxaline. 2.75 g 2.5 N NaOH was added with cooling to 1 g 2-acetylaminoquinoxaline in 20 ml Me_2CO, followed by 0.5 ml Me_2SO_4 at 0-5°, the whole left for 2 hr at 5-10°, then evaporated under reduced pressure at 18-20°, to give 0.4 g 2-(acetylmethylamino)-quinoxaline, mp 87-88°. Found: C 65.56; H 5.59; N 20.86%. Calculated for $C_{11}H_{11}N_3O$: C 65.66; H 5.51; N 20.88%.

Acid hydrolysis of 2-(acetylmethylamino) quinoxaline gave a compound identical with 2-methylaminoquinoxaline, formed by acid hydrolysis, under the same conditions, of compound VIII.

1-Methyl-2-trichloroacetylimino-1,2-dihydroquinoxaline (VI). 0.5 ml Me_2SO_4 was added at 0-5°, to a solution of 1.5 g IIId in 2.6 ml 2.5 N NaOH, the reactants held at that temperature for 1 hr 30 min-2 hr, and compound VI filtered off (0.65 g) mp 162.5-163.5°, (ex EtOH). Found: C 43.28; H 2.80; Cl 35.30; N 13.72%. Calculated for $C_{11}H_8Cl_3N_3O$: C 43.37; H 2.65; Cl 34.92; N 13.8%.

1-Methoxy-2-trichloroacetylimino-1,2-dihydroquinoxaline (VII). 0.9 ml 2.5 N NaOH, 1.8 ml water, 5 ml Me_2CO, and then 0.19 ml Me_2SO_4 were added to 0.6 g IVd at 0-5°. Then the reaction mixture was carefully triturated, first at 0-5°, then for 20 min at 20-25°, a further 0.19 ml Me_2SO_4 added, followed by additional NaOH solution to keep the pH at 8, and then the trituration was continued for 20 min at 28-30°. Yield, 0.22 g VII, purified by repeated boiling with petrol ether and then crystallizing from MeOH. Found: C 41.40; H 2.67; N 13.31%. Calculated for $C_{11}H_8Cl_3N_3O_2$: C 41.21; H 2.51; N 13.11%.

2-Amino-3-benzenesulfonyloxyquinoxaline. 0.48 ml (0.00376 mole) benzenesulfonylchloride in 5 ml dry $CHCl_3$ was added, with stirring, the temperature being held at −5 to −7°, to 0.48 g (0.003 mole) II in 3 ml dry pyridine. The temperature was maintained for 30 min more, the reaction products poured on to ice, acidified to pH 2, the mixture then extracted with $CHCl_3$. Yield, 0.4 g compound mp 180-181° (ex EtOH). The IR spectrum had bands at 3500, 3215, 3130 and 1655 cm^{-1}. Found: C 55.50; H 3.87; N 13.80; S 10.41%. Calculated for $C_{14}H_{11}N_3O_3S$: C 55.8; H 3.68; N 13.94; S 10.62%.

Hydrolysis of 2-amino-3-benzenesulfonyloxyquinoxaline. 0.15 g 2-amino-3-benzenesulfonoxyquinoxaline in 1.5 ml 2.5 N HCl was refluxed for 15 min, cooled, and water added. The resultant solution was decolorized with active charcoal, filtered, and the filtrate neutralized with 2.5 N NaOH, being brought to pH 7. Yield 0.08 g 2-amino-3-hydroxyquinoxaline, previously prepared by another method [1]. Found: N 26.28%. Calculated for $C_8H_7N_3O$: N 26.07%.

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