Reaction of Quinoxaline Derivatives with Nucleophilic Reagents

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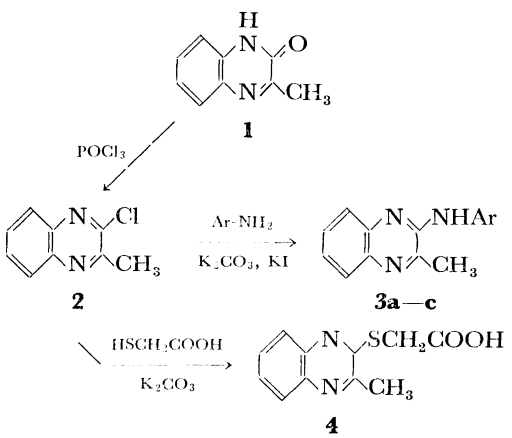
2-Chloro-3-methylquinoxaline reacts with aromatic amines in basic medium forming 2-arylamino-3-methylquinoxalines, also it reacts with mercaptoacetic acid. The 3-methyl-2(1*H*)-quinoxalinone condenses with aromatic aldehydes forming the corresponding 3-(substituted styryl)-2(1*H*)-quinoxalinones which add bromine in acetic acid to yield the corresponding dibromo derivatives which react with morpholine, sodium methoxide, and piperidine to give the corresponding compounds. 3-Methyl-2(1*H*)-quinoxalinone undergoes side-chain bromination to yield 3-bromomethyl-2(1*H*)-quinoxalinone, which reacts with aromatic amines, sodium salt of saccharine, potassium phthalimide··· 3-Methyl-2(1*H*)-quinoxalinone with P_2S_5 gave 3-methyl-2(1*H*)-quinoxalinethione which reacts with 2-aminoethanol, dimethyl sulfate, and halo acids.

2- and 3-Substituted quinoxalines were prepared by direct condensation of *o*-phenylenediamines with the proper reagents.[1] However many of such substituents could be prepared by direct substitution on the nucleus[2] or on the side chain.[3]

The present study deals with the synthesis and study of the reactivity of different 2- and 3-substituted quinoxalines and quinoxalinones towards nucleophilic substitution and condensation reactions.

3-Methyl-2(1*H*)-quinoxalinone (**1**) was prepared by condensation of *o*-phenylenediamine and sodium pyruvate.[4] The 3-methyl-2(1*H*)-quinoxalinone reacts with phosphoryl chloride[5] to yield 2-chloro-3-methylquinoxaline (**2**), whose NMR spectra showed a singlet at δ 2.85 (3H, $-CH_3$) and a multiplet centered at δ 7.85 (4H, aromatic ring).

2-Chloro-3-methylquinoxaline reacts with aromatic amines as nucleophilic reagents in dry benzene in presence of anhydrous potassium carbonate and potassium iodide forming the corresponding 2-arylamino-3-methylquinoxalines (**3a**—**c**).



The NMR of the compounds (**3a**—**c**) were in agreement with the given structures as shown in Table 1. Their IR spectra showed NH band at 3350—3200 cm^{-1}.

Similarly, 2-chloro-3-methylquinoxaline reacts with mercaptoacetic acid in presence of potassium carbonate in dry benzene to yield 2-(carboxymethylthio)-3-methylquinoxaline (**4**) whose IR spectrum showed absorption band at 1710 cm^{-1} (C=O of COOH) and a broad band between 3000—2500 cm^{-1} (associated –OH of COOH). The NMR spectrum shows a singlet at δ 2.75 (3H, $-CH_3$), a singlet at δ 4.1 (2H, $-CH_2-$), a multiplet at δ 7.85 (4H, aromatic ring) and a singlet at δ 11 (1H, –COOH).

3-Methyl-2(1*H*)-quinoxalinone undergoes condensation on fusion with aromatic aldehydes in presence of piperidine forming the corresponding 3-(substituted styryl)-2(1*H*)-quinoxalinones (**5a**—**k**). The IR spectra showed absorption band at 1620 cm^{-1} of the conjugated C=C. In UV spectra (Table 2) a bathochromic shift (red shift) of the K-band observed in 3-styryl-2(1*H*)-quinoxalinones (**5a**—**k**) as compared with the parent compound (**1**) (λ_{max} 340 nm) which was attributed to the difference in auxochromic character of the quinoxalinone ring in conjugation with –C=N– group.

o-Hydroxystyryl derivative (λ_{max} 400 nm) showed less bathochromic shift than its *p*-isomer (λ_{max} 406 nm) and this may be attributed to the steric hindrance of the bulky group at the ortho-position, thus distorting the coplanarity of the conjugated system.

The coupling constant of the styryl protons is 15—16 Hz indicating its trans configuration (Table 3).

3-(Substituted styryl)-2(1*H*)-quinoxalinones (**5a**—**k**) undergo reactions characteristic for α,β-unsaturated compounds. Bromine adds on such compounds in acetic acid to yield the corresponding dibromo derivatives **6a**—**d**. In the UV spectra of these dibromo compounds, peak near 390—396 nm corresponding to the parent styryl group **5** disappears and only absorbs in the region 346—350 nm which is closely similar to the absorption of the parent quinoxalone nucleus, confirming the absence of the sidechain conjugation at position-2. The NMR spectrum of the dibromide **6b** showed the following characteristic signals: two doublets at δ 2.42 (1H, –CH–C=N) and δ 3.23 (1H, –CH–ph); singlet at δ 6.1 (1H, NH) and symmetrical multiplet centered at 7.52 (8H, aromatic).

The effect of *p*-substituents of the phenethyl moiety of **6a**, **6b** on the halogen susceptibility towards some nucleophilic displacement reactions have been examined. The presence of an electron-donating group such as the *p*-methoxyl group in compound **6a** facilitates the removal of the bromine atoms when refluxed with ethanol to give the corresponding styryl compound. However when refluxed with morpholine in dry benzene it gave a product which contains no bromine

Table 1. NMR spectra of 2-arylamino-3-methylquinoxalines

Compd No.	Ar-	δ			
		CH_3	Aromatic	-NH-	Substituent
3a	C_6H_5	2.6(s)	7.4 —7.8(m)	8.15(s)	—
3b	p-$CH_3C_6H_4$-	2.5(s)	7.35—7.75(m)	8.00(s)	2.5(s, p-CH_3-)
3c	p-ClC_6H_4-	2.7(s)	7.35—7.8(m)	6.65(s)	—

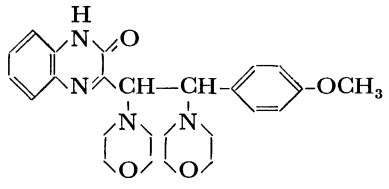
Table 2. UV spectra of 3-(substituted styryl)-2(1*H*)-quinoxalinones

Compd No.	Ar-	λ_{max}/nm	$\varepsilon \times 10^5$
1	—	340	0.09
5a	C_6H_5	390	0.155
5c	p-$CH_3C_6H_4$-	394	0.293
5d	p-$(CH_3)_2NC_6H_4$-	450	0.60
5e	p-ClC_6H_4-	390	0.438
5g	o-HOC_6H_4-	400	0.17
5h	p-HOC_6H_4-	406	0.375
5j	α-$C_{10}H_7$-	396	0.280
5k	p-$NO_2C_6H_4$-	396	0.226

Table 3. NMR spectra of 3-(substituted styryl)-2(1*H*)-quinoxalinones (**5b, d**)

Compd No.	Substituent	NH	-CH=CH-Ar		Aromatic
5b	4.0 (s) (3H, $-OCH_3$)	6.7	7.15	8.2	7.65
5d	3.15(s) (6H, $-N(CH_3)_2$	6.8	7.4	8.25	7.7

and is identified as 3-[1,2-dimorpholino-2-(p-methoxyphenyl)ethyl]-2(1*H*)-quinoxalinone (**7**).



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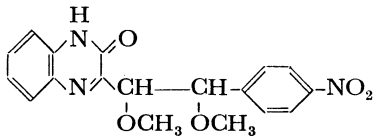
On the other hand, the presence of an electron-withdrawing group such as the p-nitro group **6d** gives an additional stability to the halogen atoms to such an extent that they are displaced by sodium methoxide in methanol to give 3-[1,2-dimethoxy-2-(p-nitrophenyl)ethyl]-2(1*H*)-quinoxalinone (**8**).



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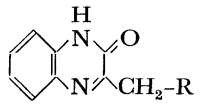
When the dibromide **6d** was refluxed with piperidine in dry dioxane, dehydrobromination of the β-bromine occurs followed by substitution of the α-bromine to give the corresponding (α-piperidinostyryl)quinoxalinone (**9**) where the IR spectrum showed absorption band at 1610 cm^{-1} of conjugated C=C. The UV spectra showed λ_{max} at 380 nm confirming the presence of conjugating styryl residue at position-3 with the quinoxalinone ring system.

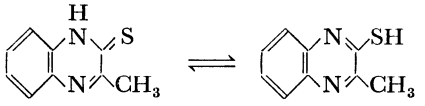
3-Methyl-2(1*H*)-quinoxalinone dissolved in acetic acid undergoes side-chain bromination in the presence of sodium acetate[6] yielding 3-bromomethyl-2(1*H*)-quinoxalinone (**10**). The latter compound reacts with p-bromoaniline and 1-naphthylamine forming the corresponding 3-arylaminomethyl-2(1*H*)-quinoxalinones (**11a, 11b**). Also it reacts with phenylhydrazine to give 3-(2-phenylhydrazinomethyl)-2(1*H*)-quinoxalinone (**12**) whose IR spectrum showed side-chain –NH– absorption band at 3380 cm^{-1}. The NMR spectrum of compound **12** showed a singlet at δ 2.4 (1H, $-CH_2-NH-$), a singlet at δ 3.3 (2H, $-CH_2-$), a singlet at δ 6.8 (1H, –NH– of quinoxalinone nucleus), a multiplet centered at δ 7.3 (9H, aromatic rings) and a singlet at δ 8.2 (1H, –NH–ph).

3-Bromomethyl-2(1*H*)-quinoxalinone reacts with the sodium salt of saccharin, potassium phthalimide, sodium p-nitrophenolate, thiophenol, silver acetate and thiourea in ethanol as a solvent to give the corresponding substituted compounds **13**, **14**, **15**, **16**, **17**, and **18** respectively.



R		R	
11a	p-BrC_6H_4NH-	**15**	O_2N-⟨○⟩-O-
11b	α-$C_{10}H_7NH$-	**16**	⟨○⟩-S-
12	C_6H_5NHNH-	**17**	CH_3COO-
13	⟨○⟩(SO₂, CO)N-	**18**	HN=C(NH₂·HBr)—S—
14	⟨○⟩(CO, CO)N-		

3-Methyl-2(1*H*)-quinoxalinone (**1**) when refluxed with phosphorus pentasulfide in dry pyridine gave 3-methyl-2(1*H*)-quinoxalinethione (**19**), where IR spectrum showed bands at 3350 cm^{-1} (NH) and 1550 cm^{-1} (C=S).



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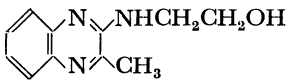
The NMR spectrum is in agreement with the thione form and showed a singlet at δ 2.8 (3H, $-CH_3$), a singlet at δ 7.25 (1H, NH) and a multiplet at δ 7.35—7.95 (4H, aromatic).

3-Methyl-2(1*H*)-quinoxalinethione (**19**) reacts with 2-aminoethanol to yield 2-(2-hydroxyethylamino)-3-methylquinoxaline (**20**).

Table 4. 3-(Substituted styryl)-2(1*H*)-quinoxalinones (**5a**—**k**)

Compd No.	Ar-	Yield %	Cryst. solvent	Mp θ_m/°C	Formula	Found (%) C	H	N	Calcd (%) C	H	N
5a	C_6H_5-	53	Dioxane	252	$C_{16}H_{12}N_2O$	—	—	11.30	—	—	11.29
5b	*p*-$CH_3OC_6H_4$-	54	Benzene	249	$C_{17}H_{14}N_2O_2$	—	—	9.98	—	—	10.07
5c	*p*-$CH_3C_6H_4$-	58	Ethanol	250	$C_{17}H_{14}N_2O$	—	—	10.71	—	—	10.68
5d	*p*-$(CH_3)_2NC_6H_4$-	83	Benzene	256	$C_{18}H_{17}N_3O$	74.23	5.71	—	74.23	5.84	—
5e	*p*-ClC_6H_4-	71	1-Butanol	276	$C_{16}H_{11}ClN_2O$	67.93	3.91	9.93	67.96	3.89	9.91
5f	C_6H_5CH=CH-	37	Ethanol	230	$C_{18}H_{14}N_2O$	78.89	5.14	—	78.83	5.11	—
5g	*o*-HOC_6H_4-	38	Ethanol	240	$C_{16}H_{12}N_2O_2$	72.69	4.69	—	72.73	4.55	—
5h	*p*-HOC_6H_4-	76	Benzene	285	$C_{16}H_{12}N_2O_2$	72.80	4.44	—	72.73	4.55	—
5i	2,4-$(OH)_2C_6H_3$-	50	Ethanol	250	$C_{16}H_{12}N_2O_3$	68.50	4.31	—	68.57	4.29	—
5j	α-$C_{10}H_7$-	17	Benzene	230	$C_{20}H_{14}N_2O$	80.50	4.3	—	80.54	4.7	—
5k	*p*-$NO_2C_6H_4$-	52	Acetic acid	310	$C_{16}H_{11}N_3O_3$	—	—	14.55	—	—	14.33



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The NMR spectrum showed a singlet at δ 2.55 (3H, CH_3), triplet at δ 3.85 (4H, $-CH_2-CH_2-$), singlet at 4.85 (1H, –OH), singlet at δ 5.42 (1H, NH) and multiplet at δ 7.65 (4H, aromatic).

The thione derivative **19** undergo *S*-alkylation, where it reacts with dimethyl sulfate in alkaline medium to give 2-methyl-3-(methylthio)quinoxaline (**21**), with chloroacetic acid to give 3-(carboxymethylthio)-2-methylquinoxaline (**4**) and with 3-bromopropionic acid to give 3-(2-carboxyethylthio)-2-methylquinoxaline (**22**). The NMR spectra of **21** showed a singlet at δ 2.65 (6H, $-CH_3$, S–CH_3) and a symmetrical multiplet centered at δ 7.75 (4H, aromatic).

2-Methyl-3-(methylthio)quinoxaline (**21**) dissolved in acetic acid undergoes side-chain bromination in presence of anhydrous sodium acetate to yield 2-bromomethyl-3-(methylthio)quinoxaline (**23**), whose NMR spectrum showed a singlet at δ 2.75 (3H, S–CH_3), a singlet at δ 4.75 (2H, $-CH_2Br$) and symmetrical multiplet centered at δ 7.85 (4H, aromatic ring).

Experimental

Melting points reported are uncorrected. Elemental analysis was carried out at the microanalytical unit of the National Research Center, El-Doky, Cairo. IR spectra were recorded on a Beckman 20 infrared spectrophotometer using KBr Wafer technique. UV spectra in ethanol were recorded on a Pye-Unicam SP 8000 spectrophotometer and NMR spectra on 90 MHz Bruker spectrospin and Varian EM-390 90 MHz.

*3-Methyl-2(1H)-quinoxalinone (**1**).*[4] White needles from benzene, mp 245 °C.

*2-Chloro-3-methylquinoxaline (**2**).*[5] Colourless needles from light petroleum, mp 86 °C.

Reaction of 2-Chloro-3-methylquinoxaline with Aromatic Amines. A mixture of 2-chloro-3-methylquinoxaline (0.01 mol) and an aromatic amine (0.012 mol) was refluxed for 10 h in dry benzene (20 ml) in presence of anhydrous potassium carbonate and potassium iodide. The reaction mixture was filtered while hot, concentrated and cooled. The separated product was recrystallized from the proper solvent.

*2-(Anilino)-3-methylquinoxaline (**3a**),* colourless needles from ethanol, mp 126—27 °C. Found: N, 17.83%. Calcd for $C_{15}H_{13}N_3$: N, 17.87%. The IR spectrum showed (NH) band at 3350 cm^{-1}.

*2-(p-Toluidino)-3-methylquinoxaline (**3b**),* gray crystals from benzene, mp 172—73 °C. Found: C, 77.08; H, 6.03%. Calcd for $C_{16}H_{15}N_3$: C, 77.11; H, 6.02%. The IR spectrum showed bands, (NH) at 3200 cm^{-1}, (C=N) at 1620 cm^{-1}.

*2-(p-Chloroanilino)-3-methylquinoxaline (**3c**),* yellow crystals from benzene, mp 124 °C. Found: N, 15.53%. Calcd for $C_{15}H_{12}ClN_3$: N, 15.58%. The IR spectrum showed bands, at 3270 cm^{-1} (NH), 1620 cm^{-1} (C=N).

*2-(Carboxymethylthio)-3-methylquinoxaline (**4**).* A mixture of 2-chloro-3-methylquinoxaline (0.01 mol) and mercaptoacetic acid (0.012 mol) was refluxed for 4 h in dry benzene (20 ml) in presence of anhydrous potassium carbonate. Solvent was evaporated and the residue was treated with dil hydrochloric acid and extracted with ether. The ethereal layer was dried and evaporated. The solid product was recrystallized from benzene as yellow crystals, mp 150 °C. Found: C, 56.46; H, 4.26; N, 11.9%. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.41; H, 4.27; N, 11.97%.

Reaction of 3-Methyl-2(1H)-quinoxalinone with Aromatic Aldehydes. 3-Methyl-2(1*H*)-quinoxalinone (**1**) (0.1 mol) and the aldehyde (0.12 mol) were fused together in presence of few drops of piperidine. The reaction product washed with petroleum ether (60—80 °C) and recrystallized from the proper solvent (Table 4).

Addition of Bromine on 3-(Substituted styryl)-2(1H)-quinoxalinone. To a cold solution of the styryl compound (0.01 mol) in glacial acetic acid (30 ml), bromine (0.01 mol) in glacial acetic acid was added gradually while stirring and the reaction mixture stirred for 1 h. The product was precipitated, filtered off, washed with glacial acetic acid and recrystallized from xylene, yield 65—75%.

*3-[1,2-Dibromo-2-(p-methoxyphenyl)ethyl]-2(1H)-quinoxalinone (**6a**),* white crystals, mp 180 °C. Found: N, 6.45; Br, 36.4%. Calcd for $C_{17}H_{11}Br_2N_2O_2$: N, 6.39; Br, 36.2%.

*3-[1,2-Dibromo-2-(p-chlorophenyl)ethyl]-2(1H)-quinoxalinone (**6b**),* white crystals, mp 255—56 °C. Found: C, 43.36; H, 2.50; N, 6.39%. Calcd for $C_{16}H_{11}Br_2ClN_2O$: C, 43.29; H, 2.48; N, 6.31%.

*3-[1,2-Dibromo-2-(m-nitrophenyl)ethyl]-2(1H)-quinoxalinone (**6c**),* white crystals, mp 275 °C. Found: C, 42.30; H, 2.58; N, 9.23%. Calcd for $C_{16}H_{11}Br_2N_3O_3$: C, 42.38; H, 2.42; N, 9.27%.

*Reaction of Nucleophiles with the Dibromides **6** to Produce the α,β-Disubstituted Products. General Procedure:* A mixture of **6** (0.01 mol) and nucleophile (0.024 mol) in solvent (40 ml) was refluxed together. The hot solution filtered, evap-

orated and the solid separated crystallized from the proper solvent.

3-[1,2-Dimorpholino-2-(p-methoxyphenyl)ethyl]-2(1H)-quinoxalinone (7). From morpholine in dry benzene; 4 h reflux, recrystallized from dioxane as yellow crystals, mp 245 °C, yield 23%. Found: N, 12.37%. Calcd for $C_{25}H_{30}N_4O_4$: N, 12.44%.

3-[1,2-Dimethoxy-2-(p-nitrophenyl)ethyl]-2(1H)-quinoxalinone (8). From sodium methoxide in methanol, 3 h reflux, recrystallized from aqueous methanol as yellow crystals, mp 265 °C, yield 29%. Found: N, 11.90%. Calcd for $C_{18}H_{17}N_3O_5$: N, 11.83%.

3-(α-Piperidino-p-nitrostyryl)-2(1H)-quinoxalinone (9). A mixture of **6d** (0.01 mol) and piperidine (0.024 mol) in dry dioxane (50 ml) was refluxed for 1 h. The hot solution was filtered and concentrated and diluted with drops of water. The separated solid was recrystallized from petroleum ether (60—80) as orange crystals, mp 232—33 °C, yield 49%. Found: N, 14.86%. Calcd for $C_{21}H_{20}N_4O_3$: N, 14.89%.

3-Bromomethyl-2(1H)-quinoxalinone (10),[6] white crystals by sublimation, mp 225 °C (decomp).

Reaction of 3-Bromomethyl-2(1H)-quinoxalinone with Aromatic Amines. A mixture of 3-bromomethyl-2(1*H*)-quinoxalinone (**10**) (0.01 mol), the aromatic amine (0.012 mol) and sodium carbonate was refluxed in ethanol (40 ml) for 3 h. The hot solution was filtered and concentrated, then diluted with few drops of water and the separated solid was recrystallized from the proper solvent.

3-(p-Bromoanilinomethyl)-2(1H)-quinoxalinone (11a), crystallized from ethanol, mp 250 °C (decomp), yield 61%. Found: C, 54.63; H, 3.62; N, 12.75%. Calcd for $C_{15}H_{12}BrN_3O$: C, 54.54; H, 3.63; N, 12.72%.

3-(1-Naphthylaminomethyl)-2(1H)-quinoxalinone (11b), crystallized from ethanol, mp 335 °C, yield 50%. Found: N, 14.04%. Calcd for $C_{19}H_{15}N_3O$: N, 14.00%.

3-(2-Phenylhydrazinomethyl)-2(1H)-quinoxalinone (12), red needles from dioxane, mp 305 °C, yield 83%. Found: C, 67.6; H, 5.22%. Calcd for $C_{15}H_{14}N_4O$: C, 67.66; H, 5.26%.

Reaction of 3-Bromomethyl-2(1H)-quinoxalinone with Organic Acid and Base Compounds. A mixture of 3-bromomethyl-2(1*H*)-quinoxalinone (**10**) (0.01 mol) and (0.012 mol) of each one of the following compounds; sodium salt of saccharin, potassium phthalimide, sodium *p*-nitrophenolate, thiophenol, silver acetate, thiourea, was refluxed for 4 h in ethanol (30 ml). The hot solution was filtered and concentrated, then diluted with few drops of water, the separated solid was recrystallized from aqueous ethanol.

N-(3-Oxo-3,4-Dihydro-2-Quinoxalinylmethyl)saccharin (13), pale brownish crystals, mp 265 °C, yield 59%. Found: N, 12.33%. Calcd for $C_{16}H_{11}N_3O_4S$: N, 12.30%. The IR spectrum showed bands at 3450 cm^{-1} (NH), 1740 cm^{-1} (C=O of saccharin), 1670 cm^{-1} (C=O of quinoxalinone).

3-(Phthalimidomethyl)-2(1H)-quinoxalinone (14), reddish crystals, mp 188 °C, yield 50%. Found: N, 13.74%. Calcd for $C_{17}H_{11}N_3O_3$: N, 13.77%. The IR spectrum showed bands at 3120 cm^{-1} (NH), 1780, 1730 cm^{-1} (2 C=O of phthalimide), 1675 cm^{-1} (C=O of quinoxalinone nucleus).

3-(p-Nitrophenoxymethyl)-2(1H)-quinoxalinone (15), yellowish crystals, mp 190 °C, yield 51%. Found: C, 60.53; H, 3.74%. Calcd for $C_{15}H_{11}N_3O_4$: C, 60.60; H, 3.70%. The IR spectrum showed bands at 3450 cm^{-1} (NH), 1670 cm^{-1} (C=O), 1610 cm^{-1} (C=N), 1520 and 1350 cm^{-1} (NO_2).

3-(Phenylthiomethyl)-2(1H)-quinoxalinone (16), pale brownish needles, mp 178 °C, yield 75%. Found: C, 67.09; H, 4.55%. Calcd for $C_{15}H_{12}N_2OS$: C, 67.16; H, 4.47%. The IR spectrum showed bands at 3150 cm^{-1} (NH), 1675 cm^{-1} (C=O), 1610 cm^{-1} (C=N).

3-(Acetyloxymethyl)-2(1H)-quinoxalinone (17), red crystals, mp 180 °C (decomp), yield 46%. Found: N, 12.82%. Calcd for $C_{11}H_{10}N_2O_3$: N, 12.84%. The IR spectrum showed bands at 3450 cm^{-1} (NH), 1740 cm^{-1} (C=O of ester), 1670 cm^{-1} (C=O of quinoxalinone).

S-(3-Oxo-3,4-dihydro-2-quinoxalinylmethyl)thiouronium Bromide (18), pale brownish needles, mp 232 °C (decomp), yield 64%. Found: C, 38.12; H, 3.54; N, 17.69; Br, 25.42%. Calcd for $C_{10}H_{11}BrN_4OS$: C, 38.09; H, 3.49; N, 17.78; Br, 25.39%. The IR spectrum showed bands at 3300 cm^{-1} (C=NH), 3200 cm^{-1} (NH of quinoxalinone nucleus), 3100—3080 cm^{-1} ($-\overset{+}{N}H_3$), 1655 cm^{-1} (C=O), 1620 cm^{-1} (C=N) and 1280 cm^{-1} (S–R).

3-Methyl-2(1H)-quinoxalinethione (19), 3-Methyl-2(1*H*)-quinoxalinone (**1**) (0.1 mol) and phosphorus pentasulfide (0.1 mol) were refluxed for 4 h in dry pyridine (100 ml). The solvent was evaporated, the residue washed with dil acetic acid, then with water and crystallized from ethanol as yellowish needles, mp 250 °C (sublm.), yield 86%. Found: C, 61.39; H, 4.71; N, 15.79%. Calcd for $C_9H_8N_2S$: C, 61.36; H, 4.54; N, 15.90%. The IR spectrum showed bands at 3350 cm^{-1} (NH), 1620 cm^{-1} (C=N), and 1500 cm^{-1} (C=S).

2-(2-Hydroxyethylamino)-3-methylquinoxaline (20), A mixture of 3-methyl-2(1*H*)-quinoxalinethione (0.01 mol) and 2-aminoethanol (0.012 mol) was refluxed in absolute ethanol (20 ml) for 2 h. The hot solution was filtered and evaporated. The product was recrystallized from ethanol as reddish crystals, mp 105—107 °C, yield 15%. Found: N, 20.76%. Calcd for $C_{11}H_{13}N_3O$: N, 20.69%. The IR spectrum showed bands at 3400 cm^{-1} (OH), 3300 cm^{-1} (NH).

2-Methyl-3-(methylthio)quinoxaline (21), Dimethyl sulfate (0.01 mol) was stirred with 3-methyl-2(1*H*)-quinoxalinethione (0.01 mol) in sodium hydroxide solution (0.01 mol in 10 ml H_2O). The reaction mixture was kept overnight. Ammonium hydroxide was added and the solid product was filtered, washed with water, recrystallized from petroleum ether (60—80) as pale brown crystals, mp 53—54 °C, yield 79%. Found: C, 63.06; H, 5.32; N, 14.47%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.26; N, 14.74%. The IR spectrum showed bands at 1620 cm^{-1} (C=N) and 1250 cm^{-1} ($S-CH_3$).

Reaction of 3-Methyl-2(1H)-quinoxalonethione with Chloroacetic Acid and 3-Bromopropionic Acid. A mixture of 3-methyl-2(1*H*)-quinoxalinethione (0.01 mol), chloroacetic acid or 3-bromopropionic acid (0.01 mol) and potassium carbonate in ethanol (20 ml) was heated for 15 min. The hot solution filtered and acidified with drops of acetic acid. The product was separated after cooling and recrystallized from the proper solvent.

2-(Carboxymethylthio)-3-methylquinoxaline (4), yellowish crystals from benzene, mp 150 °C, yield 55%. Found: S, 13.62 %. Calcd for $C_{11}H_{10}N_2O_2S$: S, 13.68%. The IR spectrum was coincident with that of reference sample.

2-(2-Carboxyethylthio)-3-methylquinoxaline (22), brownish needles from methanol, mp 194—95 °C, yield 80%. Found: S, 12.82%. Calcd for $C_{12}H_{12}N_2O_2S$: S, 12.90%. The IR spectrum showed bands at 3000—2500 cm^{-1} (associated OH of –COOH), 1730 cm^{-1} (C=O of acid).

3-Bromomethyl-2-(methylthio)quinoxaline (23), a solution of bromine (0.01 mol in 5 ml acetic acid) was added gradually while stirring to a mixture of 2-methyl-3-(methylthio)quinoxaline (0.01 mol) and anhydrous sodium acetate (0.01 mol) in acetic acid (30 ml). The reaction mixture was heated for 15 min. The reaction product was collected by filtration and recrystallized from ethanol as white needles,

mp 136 °C, yield 19%. Found: C, 44.74; H, 3.42; N, 10.12; Br, 29.45%. Calcd for $C_{10}H_9BrN_2S$: C, 44.60; H, 3.35; N, 10.40; Br, 29.74%. The IR spectrum showed bands at 1620 cm^{-1} (C=N) and 1220 cm^{-1} (S–CH_3).

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