Synthesis and Reactions of Quinoxaline Derivatives

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Reaction of 3-methyl-2(1*H*)quinoxalinone (**1**) with alkyl, benzyl, and arenesulfonyl halides in the presence of K_2CO_3 in dry acetone gave 1-substituted 3-methyl-2(1*H*)-quinoxalinones (**2a**—**g**). However **1** reacts with benzoyl chloride under the same conditions to give 3-methyl-2-quinoxalinyl benzoate, while it reacts with P_2S_5 in dry pyridine to give 3-methyl-2(1*H*)quinoxalinethione (**4**). Treatment of **4** with methy iodide in the presence of K_2CO_3 in dry acetone gave 2-methyl-3-(methylthio)quinoxaline but not 1,3-dimethyl-2(1*H*)-quinoxalinethione which has been obtained from **2a** and P_2S_5 in dry pyridine. Treatment of **4** with benzyl bromide and/or *p*-nitrobenzyl bromide in the presence of K_2CO_3 in dry acetone gave 2-benzylthio and 2-(*p*-nitrobenzylthio)-3-methylquinoxalines. Syntheses of 1-methyl-3-(substituted styryl)-2(1*H*)-quinoxalinone (**8a**—**m**) were achieved by condensation of **2a** with aromatic aldehydes. Addition of thiophenols and mercaptoacetic acid to **8** gives 1-methyl-3-[2-(substituted phenylthio)ethyl]-2(1*H*)-quinoxalinones and 1-methyl-3-[2-(substituted phenyl)-2-(carboxymethylthio)ethyl]-2(1*H*)-quinoxalinones respectively. 1,3-Dimethyl-2(1*H*)-quinoxalinone (**2a**) condensed with ketones in the presence of $ZnCl_2$ to give 1-methyl-3-[2-(substituted phenyl)-1-alkenyl]-2(1*H*)-quinoxalinones. 1-Methyl-3-(substituted styryl)-2(1*H*)-quinoxalinethiones were produced by refluxing a mixture of **8** with P_2S_5 in dry pyridine.

Quinoxaline derivatives are important as insecticides,[1] fungicides,[2,3] antibacterials,[4] and they show important biological effects.[5,6] In continuation of our earlier work[7] on quinoxaline derivatives, the present investigation deals with the synthesis of a series of new quinoxaline and quinoxalone compounds applying new procedures which are easier and afford better yields.

It has been observed in the present study that 3-methyl-2(1*H*)-quinoxalinone[8] (**1**) reacts with alkyl, benzyl, and arenesulfonyl halides in the presence of K_2CO_3 in dry acetone to give the corresponding 1-substituted 3-methyl-2(1*H*)-quinoxalinone (**2a**—**g**). These compounds showed IR absorption bands between 1665—1710 cm^{-1} for C=O group and between 1600—1610 cm^{-1} for C=N group but they did not show absorption band at 3350 cm^{-1} for NH group. The UV spectra of **2b**,**c** in ethanol were similar to that of **1** and showed three characteristic absorption bands as shown in Table 1.

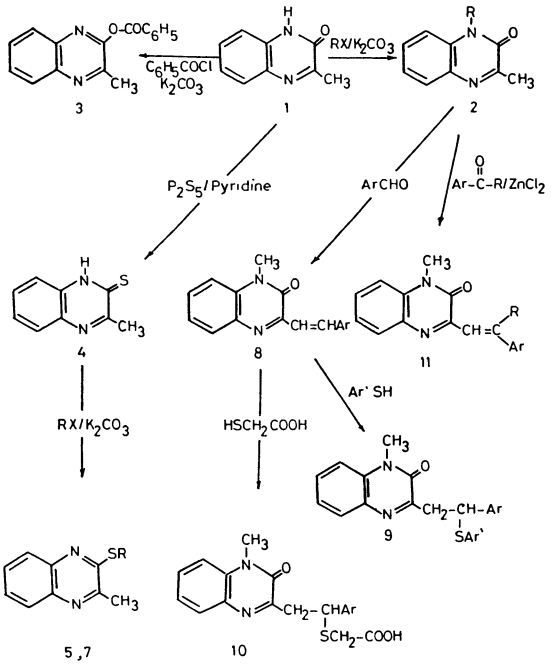
The ^{1}H-NMR spectra of compounds **2a**—**f** in $CDCl_3$ as a solvent were in agreement with the suggested structures and showed the signals given in Table 2.

However, when **1** was allowed to react with benzoyl chloride in the presence of anhydrous K_2CO_3 in dry acetone, the *O*-benzoylation was observed to give 3-methyl-2-quinoxalinyl benzoate (**3**).

The IR spectrum of **3** showed absorption band at 1740 cm^{-1} for C=O of the ester group. The NMR spectrum determined in $CDCl_3$ showed a singlet at δ 2.71 (3H, $-CH_3$), a symmetrical multiplet centered at δ 7.65 (5H, $-C_6H_5$) and a symmetrical multiplet centered at δ 8.2 (4H, aromatic protons of quinoxalinone nucleus).

Reaction of **1** with P_2S_5 in dry pyridine gave 3-methyl-2(1*H*)-quinoxalinethione (**4**), whose structure was confirmed by its IR spectrum which showed bands at 3350 cm^{-1} (NH) and at 1550 cm^{-1} (C=S).

Treatment of 3-methyl-2(1*H*)quinoxalinethione (**4**) with methyl iodide in the presence of K_2CO_3 in dry acetone gave 2-methyl-3-(methylthio) quinoxaline[9] (**5**). However, 1,3-dimethyl-2(1*H*)-quinoxalinethione (**6**) was not detected among the products. Compound **6** was prepared by reaction of 1,3-dimethyl-2(1*H*)-quinoxalinone (**2a**) with P_2S_5 in pyridine. However this observation does not exclude the possibility that 3-methyl-2(1*H*)-quinoxalinethione (**4**) exists in solution as 2-mercaptoquinoxaline rather than as cyclic thioamide tautomer. This was further confirmed by the similarity of the UV spectra of **6** together with that of compound **4** and their subsequent difference from that corresponding to 2-methyl-3-(methylthio)quinoxaline (**5**) (Table 3). The structures of **5** and **6** were further confirmed by NMR spectra in $CDCl_3$. Compound **5** showed a singlet at δ 2.68 (6H, $-S-CH_3$ and $-C-CH_3$) and a symmetrical multiplet centered at δ 7.8 (4H, aromatic protons), where compound **6** showed a singlet at δ 2.82 (3H, $-C-CH_3$), a singlet at δ 4.2 (3H, $N-CH_3$) and a multiplet at δ 7.4—7.9 (4H, aromatic protons).



Scheme 1.

Treatment of 3-methyl-2(1*H*)-quinoxalinethione (**4**)

Table 1. UV spectral data of some 1-substituted 3-methyl-2(1*H*)-quinoxalinones

No.	R	Band I		Band II		Band III	
		λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$
1	H	278	2000	328	2300	338	1750
2b	$-CH_2C_6H_5$	282	2700	330	2900	338	2500
2c	$-CH_2C_6H_4CH_3(p)$	282	2900	330	3100	338	2500

Table 2. ^{1}H-NMR spectral data for 1-substituted 3-methyl-2(1*H*)-quinoxalinones (**2a—f**)

No.	R	N=C-CH_3	N-CH_2-Ar	Aromatic protons	N-Ar-$CH_3(p)$
2a	$-CH_3$	2.60	3.7(CH_3)	7.15—7.9 (4H)	—
2b	$-CH_2C_6H_5$	2.65	5.50	7.15—7.9 (9H)	—
2c	$-CH_2C_6H_4CH_3(p)$	2.65	5.45	7.05—7.9 (8H)	2.25
2e	$-SO_2C_6H_5$	2.75	—	7.60—8.35 (9H)	—
2f	$-SO_2C_6H_4CH_3(p)$	2.75	—	7.30—8.25 (8H)	2.50

In the above reactions substitution occurred favorably at the NH group.

Table 3. UV spectral data of substituted 2(1*H*)-quinoxalinethiones (**4**, **6**) and 2-(benzylthio)quinoxalines (**5**, **7**)

No.	Band I		Band II		Band III		Band IV	
	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε $dm^3\ mol^{-1}\ cm^{-1}$
4	216	17100	278	9400	396	5400	—	—
5	235	10600	262	10600	345	6900	354	6800
6	217	22500	274	15800	390	8600	—	—
7a	238	7700	266	7150	347	4300	356	4150
7b	240	8700	266	10900	343	4250	355	4100

with benzyl bromide and/or *p*-nitrobenzyl bromide in the presence of K_2CO_3 in dry acetone gave 2-benzylthio and 2-(*p*-nitrobenzylthio)-3-methylquinoxalines (**7a**,**b**) respectively. Their electronic absorption spectra were similar with that of **5** (Table 3).

The ^{1}H-NMR spectrum of **7b** in CF_3 COOH showed a singlet at δ 2.55 (3H, -C-CH_3), a singlet at δ 4.35 (2H, -S-CH_2-) and a multiplet at δ 7.2—7.8 (8H, aromatic protons).

The reactivity of the 3-methyl group towards condensation reaction into the corresponding styryl compounds **8** was demonstrated either by: (A) Fusion of 1,3-dimethyl-2(1*H*)-quinoxalinone (**2a**) with the corresponding aldehyde in the presence of few drops of piperidine or (B) refluxing **2a** with the corresponding aldehyde in dry pyridine using few drops of piperidine and (C) refluxing **2a** with the corresponding aldehyde in acetic anhydride. The IR spectra of compounds **8a—m** showed bands at 1665—1650 cm^{-1} for C=O group, at 1630—1610 cm^{-1} for C=C group and at 1580 cm^{-1} C=N. It is suggested that compounds **8** are of trans configuration since a strong absorption band appeared in the region 990—980 cm^{-1} characteristic of trans olefinic configuration. The coupling constants of the styryl protons in the NMR spectra are 15—16 Hz, confirming its trans configuration.

The UV spectra of the styryl compounds (**8a**,**b**,**d**,**e**) showed a bathochromic shift of the K-band as compared with that of the parent compound (**2a**). This shift has been attributed to the difference in auxochromic character of the styryl residue at position-3 of the quinoxalinone ring in conjugation with -C=N- group. *o*-Nitrostyryl derivative (**8j**) showed less bathochromic shift than its *p*-isomer (**8i**) due to the steric hindrance at ortho-position distorting the coplanarity and conjugation (Table 4).

Table 4. UV spectral data of 1-methyl-3-styryl-2(1*H*)-quinoxalinones (**8**)

No.	Ar	λ_{max}/nm	ε/$dm^3\ mol^{-1}\ cm^{-1}$
8a	$-C_6H_5$	384	7350
8b	$-C_6H_4OCH_3(p)$	404	8800
8d	$-C_6H_4N(CH_3)_2(p)$	452	9400
8e	$-C_6H_4OH(p)$	402	6950
8i	$-C_6H_4NO_2(p)$	402	9250
8j	$-C_6H_4NO_2(o)$	394	6000

Thiophenols were added to 1-methyl-3-(substituted styryl)-2(1*H*)-quinoxalinones (**8**) to produce 1-methyl-3-[2-(substituted phenyl)-2-(substituted phenylthio)-ethyl]-2(1*H*)-qunoxalinones (**9a—e**) whose IR spectra showed band at 1670 cm^{-1} for C=O group and revealed the disappearance of C=C band at 1620—1610 cm^{-1}. The UV spectrum of **9b** in ethanol showed absorption band at λ_{max} 340 nm (ε 1800) which is close to that of **2a** λ_{max} 340 nm (ε 5500) confirming the saturation of the styryl side chain. The ^{1}H-NMR spectrum of **9b** in

Table 5. 1-Substituted 3-methyl-2-(1*H*)-quinoxalinones (**2**)

No.	1-Substituent	Mp θ_m/°C	Crystal. solvent	Yield %	Mol formula	Found (%)			Calcd (%)		
						C	H	N	C	H	N
2a	CH_3	84— 85[a)]	Pet. ether (60—80 °C)	65	$C_{10}H_{10}N_2O$	68.83	5.80	16.13	68.95	5.79	16.08
2b	$C_6H_5CH_2$-	87— 88	Pet. ether (40—60 °C)	90	$C_{16}H_{14}N_2O$	76.95	5.25	11.19	76.78	5.64	11.19
2c	*p*-$CH_3C_6H_4CH_2$-	174—175	Pet. ether (60—80 °C)	85	$C_{17}H_{16}N_2O$	77.19	6.09	10.59	77.25	6.10	10.60
2d	*p*-$NO_2C_6H_4CH_2$-	212—213	Acetone	65	$C_{16}H_{13}N_3O_3$	65.12	4.51	14.32	65.08	4.44	14.23
2e	$C_6H_5SO_2$-	126—127	Pet. ether (60—80 °C)	90	$C_{15}H_{12}N_2O_3S$	60.10	4.33	9.26	60.00	4.03	9.33
2f	*p*-$CH_3C_6H_4SO_2$-	109—110	Ethanol	89	$C_{16}H_{14}N_2O_3S$	61.15	4.50	8.81	61.14	4.49	8.91
2g	2-$C_{10}H_7SO_2$-	126—127	Acetone	90	$C_{19}H_{14}N_2O_3S$	65.37	4.21	8.09	65.14	4.03	8.00

Compounds are colorless crystals except **2e—g** are brownish crystals. a) Not changed by admixture with the reference sample.[10)]

$CDCl_3$ showed a singlet at δ 3.38 (3H, *N*-CH_3), a doublet at δ 3.58 (2H, -CH_2-side chain), a singlet at δ 3.7 (3H, -OCH_3), a triplet at δ 4.35 (1H, -CH-side chain). J_{vic} 6—7 Hz and a multiplet at δ 6.7—7.85 (13H, aromatic protons). Mercaptoacetic acid underwent addition to 1-methyl-3-styryl-2(1*H*)-quinoxalinones (**8a—c, i**) giving the products, 1-methyl-3-[2-(carboxymethylthio)-2-(substituted phenyl)ethyl]-2(1*H*)-quinoxalinones (**10a—d**). The IR spectra of **10a,c** showed bands at 1650 cm^{-1} (C=O) of quinoxalinone nucleus, at 1720 cm^{-1} (C=O) of carboxylic acid and a broad band at 2700—2500 cm^{-1} (assoc. OH). The UV spectrum of **10a** in ethanol showed a band at λ_{max} 343 nm (ε 2000) which is close to λ_{max} 340 nm (ε 5500) of the compound **2a**. The NMR spectrum of **10a** in $CDCl_3$ showed a singlet at δ 3.15 (2H, -CH_2-carboxyl); a doublet at δ 3.6 (2H-CH_2- to quinoxalinone nucleus), a singlet at δ 3.85 (3H, *N*-CH_3), a triplet at δ 4.80 (1H, -CH-side-chain), J_{vic} 6—7 Hz and a multiplet at δ 7.2—8 (9H, aromatic protons).

1,3-Dimethyl-2(1*H*)-quinoxalinone (**2a**) condensed with ketones, such as, acetophenone, *p*-bromo-, *p*-methyl-, *p*-methoxy acetophenones, and benzophenone, in the presence of zinc chloride gave 1-methyl-3-[2-(substituted phenyl)-1-alkenyl]-2(1*H*)-quinoxalinones (**11a—e**). The NMR spectrum of compound **11e** in $CDCl_3$ showed a singlet at δ 3.7 (3H, *N*-CH_3), a singlet at δ 6.85 (1H, -CH=) and a multiplet at δ 7.35—7.65 (14H, aromatic protons).

Syntheses of 1-methyl-3-(substituted styryl)-2(1*H*)-quinoxalinethiones (**12a—e**) were achieved by refluxing a mixture of **8** with P_2S_5 in dry pyridine for 5 h. In the IR spectrum of compound **12d** C=O Stretching disappeared, while two new bands at 1515, 1240 cm^{-1} for C=S group and also a band at 1610 cm^{-1} for C=C group was observed. The UV spectrum of compound **12d** in $CHCl_3$ showed a bathochromic shift for the K-band at λ_{max} 442 nm (ε 135×10^2) in comparison with its precursor 1,3-dimethyl-2(1*H*)-quinoxalinethione (**6**), λ_{max} 390 nm (ε 86×10^2), which proves the extended conjugation between the styryl residue and -C=N- group of 2(1*H*)-quinoxalinethione nucleus.

Experimental

Melting points reported are uncorrected. IR spectra were recorded on a Beckman 20 infrared spectrophotometer using KBr Wafer technique. UV spectra in ethanol on a Pye-Unicam SP 8000 Spectrophotometer and NMR spectra were recorded on a 90 MHz Bruker spectrospin and a Varian EM-390 spectrometer.

*3-Methyl-2(1*H*)-quinoxalinone (**1**).*[8)] Colorless crystals from ethanol, mp 245 °C (sublim). NMR exhibit a singlet at δ 2.9 (3H, -CH_3), a multiplet at δ 7.4—8.15 (4H, aromatic protons), while the NH proton at δ 7.1 disappeared by adding D_2O.

*Reactions of 3-Methyl-2(1*H*)-quinoxalinone (**1**) with Alkyl, Benzyl, and Arenesulfonyl Halides. General Procedure*: A mixture of 3-methyl-2(1*H*)-quinoxalinone (**1**) (0.01 mol), alkyl, benzyl, or arenesulfonyl halides (0.012 mol), and anhydrous K_2CO_3 were refluxed together for several hours in dry acetone (30 ml). The resultant *N*-substituted derivatives (**2a—g**) were crystallized from the proper solvent (Table 5).

*Synthesis of 3-Methyl-2-quinoxalinyl Benzoate (**3**).* A mixture of 3-methyl-2(1*H*)-quinoxalinone (**1**) (0.01 mol) in dry acetone, anhydrous K_2CO_3 (0.012 mol), and benzoyl chloride (0.012 mol) was heated for several hours. Acetone solution was filtered and evaporated. The product was crystallized from petroleum ether (60—80 °C) to give **3** as yellowish crystals, mp 110—111 °C, yield 2.3 g (90%). Found: C, 72.69; H, 4.68; N, 10.49%. Calcd for $C_{16}H_{12}N_2O_2$ C, 72.71; H, 4.58; N, 10.60%.

*Synthesis of 3-Methyl-2(1*H*)-quinoxalinethione (**4**).* A mixture of 3-methyl-2(1*H*)-quinoxalinone (**1**) (0.01 mol) and P_2S_5 (0.01 mol) was refluxed in dry pyridine (20 ml) for 5 h. The solvent was evaporated and the residue was treated with dil acetic acid. The solid product was filtered and crystallized from absolute ethanol to give **4** as orange-brown crystals, mp 250—251 °C (sublim), yield 1.4 g (85%). Found: C, 61.56; H, 4.59; N, 15.95%. Calcd for $C_9H_8N_2S$: C, 61.36; H, 4.58; N, 15.90%.

*Reaction of 3-Methyl-2(1*H*)-quinoxalinethione (**4**) with Alkyl and Benzyl Halides. General Procedure*: A mixture of 3-methyl-2(1*H*)-quinoxalinethione (**4**) (0.01 mol) in dry acetone, anhydrous K_2CO_3 (0.012 mol) and the corresponding alkyl or benzyl halide was heated on a steam bath for 4 h. Acetone solution was filtered and evaporated and the product was crystallized from suitable solvent.

*2-Methyl-3-(methylthio)quinoxaline (**5**)*: Colorless crystals from pet. ether (40—60 °C), mp 55—56 °C, yield 1.8 g

Table 6. 1-Methyl-3-(substituted styryl)-2(1*H*)-quinoxalinones (**8**)

No.	3-Substituent	Mp θ_m/°C	Yield %	Procedure	Mol formula	Found (%)			Calcd (%)		
						C	H	N	C	H	N
8a	$C_6H_5CH=CH-$	164—165	85	A	$C_{17}H_{14}N_2O$	78.05	5.54	10.63	77.84	5.38	10.67
8b	*p*-$CH_3OC_6H_4CH=CH-$	134—135	65	B, C	$C_{18}H_{16}N_2O_2$	73.86	5.62	9.30	73.95	5.53	9.58
8c	*p*-$CH_3C_6H_4CH=CH-$	149—150	75	A	$C_{18}H_{16}N_2O$	78.47	5.89	10.05	78.23	5.84	10.14
8d	*p*-$(CH_3)_2NC_6H_4CH=CH-$	197—198	83	A	$C_{19}H_{19}N_3O$	74.74	6.29	13.75	74.73	6.27	13.76
8e	*p*-$HOC_6H_4CH=CH-$	272—273	65	A	$C_{17}H_{14}N_2O$	73.35	5.11	10.01	73.36	5.07	10.07
8f	*o*-$HOC_6H_4CH=CH-$	249—250	65	A	$C_{17}H_{14}N_2O_2$	73.22	5.13	9.97	73.36	5.07	10.07
8g	*p*-$ClC_6H_4CH=CH-$	169—170	85	A	$C_{17}H_{13}N_2OCl$	68.75	4.50	—	68.80	4.42	—
8h	*p*-$BrC_6H_4CH=CH-$	183—184	90	A	$C_{17}H_{13}N_2OBr$	59.79	4.05	—	59.84	3.84	—
8i	*p*-$NO_2C_6H_4CH=CH-$	235—236	85	A, C	$C_{17}H_{13}N_3O_3$	66.29	4.19	13.48	66.04	4.26	13.68
8j	*o*-$NO_2C_6H_4CH=CH-$	155—156	80	A	$C_{17}H_{13}N_3O_3$	66.32	4.30	13.70	66.04	4.26	13.68
8k	*m*-$NO_2C_6H_4CH=CH-$	184—185	65	A	$C_{17}H_{13}N_3O_3$	66.31	4.40	13.57	66.04	4.26	13.68
8l	1-$C_{10}H_7CH=CH-$	168—169	75	A	$C_{21}H_{16}N_2O$	80.69	5.30	8.89	80.75	5.16	8.97
8m	2-$C_{10}H_7CH=CH-$	221—222	65	A	$C_{21}H_{16}N_2O$	80.67	5.30	9.01	80.75	5.16	8.97

All compounds crystallized from ethanol solvent, except **8f** from acetic acid. All compounds are yellow crystals, except **8d** bright deep red, **8e** bright brown, and **8h** orange crystals.

Table 7. 1-Methyl-3-[2-(carboxymethylthio)-2-(substituted phenyl)ethyl]-2(1*H*)-quinoxalinone (**10**)

No.	2-Substituent on ethyl	Mp θ_m/°C	Yield %	Mol formula	Found (%)			Calcd (%)		
					C	H	N	C	H	N
10a	C_6H_5-	169—170	80	$C_{19}H_{18}N_2O_3S$	64.52	5.20	7.82	64.40	5.12	7.91
10b	*p*-$CH_3C_6H_4-$	171—172	75	$C_{20}H_{20}N_2O_3S$	65.35	5.58	7.50	65.21	5.47	7.61
10c	*p*-$CH_3OC_6H_4-$	105—106	75	$C_{20}H_{20}N_2O_4S$	62.70	5.23	8.60	62.49	5.24	8.32
10d	*p*-$NO_2C_6H_4-$	118—119	85	$C_{19}H_{17}N_3O_5S$	57.35	4.33	10.48	57.14	4.29	10.52

All compounds are yellowish crystals from pet. ether (40—60 °C).

(95%). Found: C, 63.19; H, 5.35; N, 14.90%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.30; N, 14.74%.

*2-Benzylthio-3-methylquinoxaline (**7a**)*: Colorless crystals from acetone, mp 84—85 °C, yield 2.4 g (90%). Found: C, 72.25;H, 5.34; N, 10.56; S, 12.00%. Calcd for $C_{16}H_{14}N_2S$: C, 72.16; H, 5.30; N, 10.52; S, 12.02%.

*Synthesis of 1,3-Dimethyl-2(1H)-quinoxalinone (**6**)*: From 1,3-dimethyl-2(1*H*)-quinoxalinone (**2a**) and P_2S_5 following the same procedure for the synthesis of **4**. Brown crystals from ethanol, mp 146—147 °C, yield 85%. Found: C, 63.20; H, 5.40; S, 16.90%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.30; S, 16.82%.

*Synthesis of 1-Methyl-3-substituted Styryl-2(1H)-quinoxalinone (**8**). Procedure (A)*: In the presence of piperidine; 1,3-Dimethyl-2(1*H*)-quinoxalinone (**2a**) (0.01 mol) was fused with the corresponding aromatic aldehyde (0.012 mol) for 10 min in the presence of few drops of piperidine. The product was isolated from the reaction mixture by adding ethanol, filtered and crystallized from the proper solvent (Table 6).

Procedure (B): In the presence of pyridine solvent and piperidine; 1,3-Dimethyl-2(1*H*)-quinoxalinone (**2a**) (0.01 mol) and the appropriate aromatic aldehyde (0.012 mol) were refluxed together in dry pyridine as solvent in the presence of few drops of piperidine for 3 h after which the excess solvent was removed and the product was crystallied from suitable solvent.

Procedure (C): In acetic anhydride solvent; 1,3-Dimethyl-2(1*H*)-quinoxalinone (**2a**) (0.01 mol) and the appropriate aromatic aldehyde (0.012 mol) were refluxed together in acetic anhydride as solvent for 20 h after which the excess solvent was removed and the reaction mixture was treated as usual.

*Addition of Substituted Thiophenol to 1-Methyl-3-(substituted styryl)-2(1H)-quinoxalinone (**8**). General Procedure*: A mixture of 1-methyl-3-(substituted styryl)-2(1*H*)-quinoxalinone (**8**) (0.002 mol) and substituted thiophenol (0.004 mol) was heated at 100 °C for 2 h. The yellow-brown oil formed was triturated with pet. ether (40—60 °C) and the products obtained were crystallized from the proper solvent.

*1-Methyl-3-[2-phenyl-2-(phenylthio)ethyl]-2(1H)-quinoxalinone (**9a**)*: Colorless crystals from pet. ether (60—80 °C), mp 129—130 °C, yield 0.5 g (65%). Found: C, 74.09; H, 5.50; N, 7.45%. Calcd for $C_{23}H_{20}N_2S$: C, 74.17; H, 5.41; N, 7.52%.

*1-Methyl-3-[2-(p-methoxyphenyl)-2-(phenylthio)ethyl]-2(1H)-quinoxalinone (**9b**)*: Yellow crystals from pet. ether (40—60 °C), mp 154—155 °C, yield 0.6 g (70%). Found: C, 71.64; H, 5.60; N, 6.97%. Calcd for $C_{24}H_{22}N_2O_2S$: C, 71.62; H, 5.51; N, 6.96%.

*1-Methyl-3-[2-(p-nitrophenyl)-2-(phenylthio)ethyl]-2(1H)-quinoxalinone (**9c**)*: Yellowish crystals from pet. ether (40—60 °C), mp 141—142 °C, yield 0.45 g (55%). Found: C, 66.09; H, 4.57; N, 10.03%. Calcd for $C_{23}H_{19}N_3O_3S$: C, 66.18; H, 4.59; N, 10.07%.

*1-Methyl-3-[2-(p-methoxypenyl)-2-(p-methylphenylthio)ethyl-2(1H)-quinoxalinone (**9d**)*: Yellowish crystals from benzene and pet. ether (40—60 °C) mixture, mp 162—164 °C, yield 0.6 g (75%). Found: C, 72.13; H, 5.82; N, 6.69; S, 7.46%. Calcd for $C_{25}H_{24}N_2O_2S$: C, 72.10; H, 5.81; N, 6.73; S, 7.68%.

*1-Methyl-3-[2-(p-methoxyphenyl)-2-(o-aminophenylthio)ethyl-2(1H)-quinoxalinone (**9e**)*: Yellowish crystals from benzene and pet. ether (60—80 °C) mixture, mp 109—110 °C, yield

Table 8. 1-Methyl-3-[2-(substituted phenyl)-1-alkenyl]-2(1*H*)-quinoxalinones (**11**)

No.	2-Substituent on ethyl	Mp θ_m/°C	Yield %	Mol formula	Found (%)			Calcd (%)		
					C	H	N	C	H	N
11a	CH_3, C_6H_5-	182—183	65	$C_{18}H_{16}N_2O$	78.50	6.07	10.01	78.23	5.84	10.14
11b	CH_3, *p*-BrC_6H_4-	112—113	55	$C_{18}H_{15}N_2OBr$	60.85	4.40	8.02	60.79	4.22	7.88
11c	CH_3, *p*-$CH_3C_6H_4$	213—214	65	$C_{19}H_{18}N_2O$	78.72	6.50	9.44	78.59	6.25	9.65
11d	CH_3, *p*-$CH_3OC_6H_4$-	229—232	70	$C_{19}H_{18}N_2O$	74.59	5.97	9.07	74.49	5.92	9.15
11e	C_6H_5, C_6H_5-	189—190	85	$C_{23}H_{18}N_2O$	81.75	5.50	8.09	81.63	5.36	8.28

a) Crystallized from acetone.

Table 9. 1-Methyl-3-(substituted styryl)-2-(1*H*)-quinoxalinethiones (**12**)

No.	3-Substituent	Mp θ_m/°C	Yield %	Mol formula	Found (%)			Calcd (%)		
					C	H	S	C	H	S
12a	C_6H_5CH=CH-	170 (decomp)	50	$C_{17}H_{14}N_2S$	73.30	5.20	11.50	73.36	5.07	11.50
12b	*p*-$CH_3C_6H_4CH$=CH-	209—210	83	$C_{18}H_{16}N_2S$	73.85	5.53	10.91	73.95	5.52	10.95
12c	*p*-BrC_6H_4CH=CH-	240—241	50	$C_{17}H_{13}N_2SBr$	57.20	3.69	8.97	57.14	3.64	8.96
12d	*p*-$(CH_3)_2NC_6H_4CH$=CH-	273—274	85	$C_{19}H_{19}N_3S$	71.04	5.98	9.97	71.01	5.96	9.96
12e	*p*-$CH_3OC_6H_4CH$=CH-	194—195	75	$C_{18}H_{16}N_2OS$	70.20	5.24	10.40	70.11	5.23	10.38

All compounds crystallized from ethanol, except **12c** and **12d** from benzene. Compounds **12a, b** are black fluorescence, **12d, e** are brown fluorescence, and **12c** is dark green crystals.

0.75 g (75%). Found: C, 69.69; H, 5.60; N, 9.68%. Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.91; H, 5.40; N, 9.79%.

*Addition of Mercaptoacetic Acid to 1-Methyl-3-(substituted styryl)-2(1H)-quinoxalinone (**8**).* *General Procedure*: A mixture of 1-methyl-3-(substituted styryl)-2(1*H*)-quinoxalinone (**8**) (0.002 mol) and mercaptoacetic acid (0.002 mol) was heated at 100 °C for 2 h. The yellow oil formed was triturated with pet. ether (40—60 °C) and the products obtained were crystallized from the suitable solvent (Table 7).

*Condensation of 1,3-Dimethyl-2(1H)-quinoxalinone (**2a**) with Alkyl Aryl Ketones and Biaryl Ketones.* *General Procedure*: A mixture of 1,3-dimethyl-2(1*H*)-quinoxalinone (**2a**) (0.01 mol) and the appropriate ketone (0.01 mol) was heated under reflux in the presence of anhydrous $ZnCl_2$ (0.5 g) at 180—200 °C for 3 h, the reaction mixture was cooled, extracted with ethanol, filtered and concentrated whereby the corresponding product was obtained as brown crystals by crystallization from ethanol (Table 8).

*Synthesis of 1-Methyl-3-(substituted styryl)-2(1H)-quinoxalinethiones (**12a—e**).* *General Procedure*: A mixture of **8** (0.002 mol) and P_2S_5 (0.003 mol) was refluxed in dry pyridine (30 ml) for 5 h. The solvent was evaporated and the residue was treated with dilute acetic acid. The product was filtered and crystallized from the suitable solvent (Table 9).

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