

C, 67.95; H, 3.40; N, 17.33.

7-Chloro-4-hydroxy-5-phenyl-2,3,4,5-tetrahydro-1H-1,4-benzodiazepine (15).⁶ A solution of 3.3 g (0.01 mol) of 7-chloro-2-(*N*-nitrosomethylamino)-5-phenyl-3H-1,4-benzodiazepine 4-oxide (2) in 10 ml of tetrahydrofuran was added to a suspension of 2 g (0.05 mol) of lithium aluminum hydride in 50 ml of ether cooled to -20° . The mixture was stirred at -20 to -15° for 15 min and 10 ml of water was added cautiously. The inorganic material was separated by filtration; the filtrate was dried over sodium sulfate and evaporated. Crystallization of the residue from 2-propanol yielded 2.2 g of product with mp and mmp 167–169 $^{\circ}$.

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62-3; **8**, 53216-81-2; **9**, 53216-82-3; **11**, 53216-83-4; **12a**, 51483-10-4; **12b**, 51483-05-7; **13**, 53216-84-5; **14a**, 53216-85-6; **14b**, 53216-86-7; **14b** hemidioxonate, 53216-87-8; **15**, 1803-98-1; **16a**, 53216-88-9; **16b**, 53216-89-0; methanol, 67-56-1; allyl alcohol, 107-18-6; 2-dimethylaminoethanol, 108-01-0; hydrazine, 302-01-2; methylhydrazine, 60-34-4; formaldehyde, 50-00-0; acetic anhydride, 108-24-7; acetylhydrazine, 1068-57-1; aziridine, 151-56-4; ethanethiol, 75-08-1; hydroxylamine hydrochloride, 5470-11-1; methoxyamine hydrochloride, 593-56-6; guanidine hydrochloride, 15827-40-4.

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Quinoxaline 1,4-Dioxides. Substituent Effects on the Reaction of Benzofurazan 1-Oxides with Carbonyl Compounds^{1a}

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Two types of reactions were used to study the effect of substituents (CH_3 , OCH_3 , and CO_2CH_3) on the condensation of 5(6)-substituted benzofurazan 1-oxides with acetyl methyl sulfide (BFO reaction, A), and 4-substituted *o*-quinone dioximes with pyruvaldehyde (OQD reaction, B). Each reaction allowed the isolation of only one of the two possible isomers and the study of its nmr properties. The nitrogen atom is an electrophile in reaction A and a nucleophile in reaction B. Thus the same substituent is expected and does favor the formation of opposite ratios of 6:7 isomeric substituted quinoxaline hydroxamic acid esters 4. The ratios were determined from nmr spectra of these esters where the chemical shifts of the H-5 and H-8 protons, unlike their counterparts in quinoxaline 1,4-dioxides, are assignable. The results are interpreted by assuming that benzofurazan 1-oxides react in their ortho dinitroso tautomeric forms.

A few years ago, an elegant method for the preparation of quinoxaline 1,4-dioxides was reported. It involved a condensation of benzofurazan 1-oxide (BFO) with either enamines or enolate anions.^{2,3} Although the exact mechanism was not elucidated, initial attack at either one of the two nitrogen atoms of BFO followed by cyclization with concomitant elimination of amines, in the former, and water, in the latter, would explain the experimental results. Partial support for this mechanism came from the isolation of dihydroquinoxaline 1,4-dioxide which is a suggested intermediate in the above mechanism.⁴

Only one quinoxaline 1,4-dioxide can be obtained when a carbonyl compound, which under the reaction conditions forms one enolic form, is condensed with unsubstituted BFO. However, a mixture of 6- and 7-substituted quinoxaline 1,4-dioxide isomers is expected when 5(6)-substituted BFO's are used. Indeed such a case has been reported when 5(6)-trifluoromethyl BFO was condensed with acetyl acetone.⁵

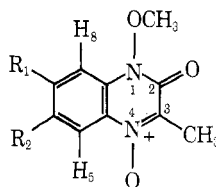
Contradictory reports concerning reactions of other 5(6)-substituted BFO's with various ketones have also appeared. While Haddadin and coworkers claimed the formation of mixture of isomers when the 5(6)-substituted BFO's (1a, 1b, and 1d) were condensed with benzoylacetophenone,⁶ Mason and Tennant reported the isolation of only the 7-substituted quinoxaline 1,4-dioxide when BFO's (1b, 1d, and 1e) were allowed to react with benzoylacetone.⁷ Later results partially supported the above claims. While

the condensation of β -keto esters with 5(6)-chloro-BFO (1d) was found to give a mixture of the corresponding 6- and 7-chloroquinoxaline 1,4-dioxides, 5(6)-methoxy-BFO (1b) furnished the 7-methoxy isomer only.⁸ In the present work a rigorous study of isomer formation was made in which the electronic effects of a 5(6) substituent on the course of BFO reaction with acetyl methyl sulfide is reported.

Determination of isomer ratios in 6(7)-substituted quinoxaline 1,4-dioxides is not an easy task since both isomers have very similar spectral and chromatographic properties. Their conversion to other derivatives where H-5 and H-8, unlike their counterparts in the parent compounds, are in different chemical environment allows full structural determination by nmr. Such a conversion has been reported earlier when 2-cyano-3-phenyl-7-substituted quinoxaline 1,4-dioxides were treated with sodium ethoxide to furnish the corresponding hydroxamic acids.⁷ In the present compounds (2a, 2b, and 2c) treatment with aqueous potassium hydroxide furnished the highly insoluble hydroxamic acids (3) followed by conversion to the esters (4) made possible their structural assignment by examining the aromatic region in the nmr spectra (Scheme I). Unlike the earlier method, these compounds have no other aromatic protons which could complicate spectral analyses.

Scheme I depicts two types of reactions (A and B) used to determine substituent effects; a BFO reaction (A) in which the nitrogen atom is an electrophile, and a condensa-

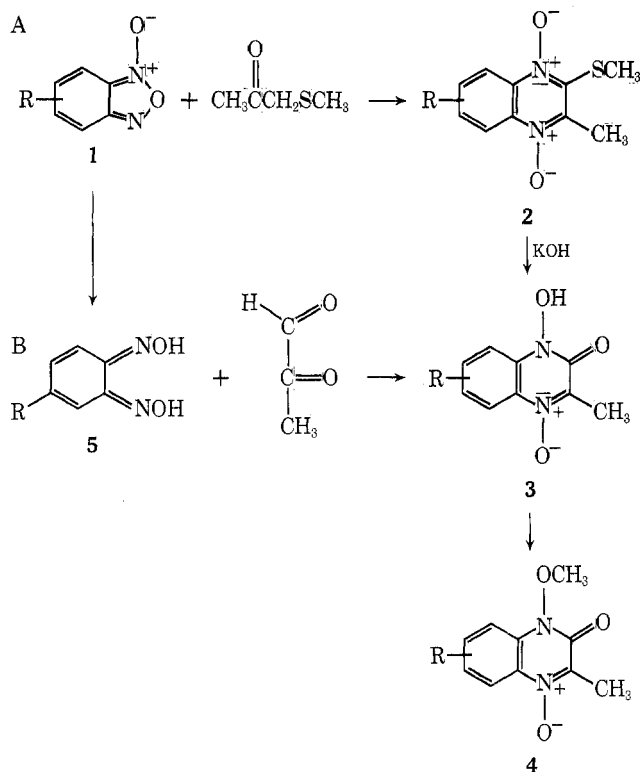
Table I
Chemical Shifts of the Hydroxamic Acid Esters^a



R ₁	R ₂	H-5	H-6	H-7	H-8	1-OCH ₃	3-CH ₃	6 or 7 subs
H	OCH ₃	7.9		7.31	7.61	4.18	2.57	3.95
OCH ₃	H	8.33	6.98		6.98	4.17	2.53	3.98
H	CH ₃	8.23		7.2	7.2	4.16	2.53	2.50
				7.6	7.6			
CH ₃	H	8.23	7.2		7.4	4.16	2.53	2.53
H	CO ₂ CH ₃	9.17		8.45	7.8	4.25	2.63	4.06
CO ₂ CH ₃	H	8.61	8.15		8.4	4.26	2.63	4.06

^a Determined in CDCl₃ and expressed in parts per million downfield from TMS. The expected multiplets with the usual ortho, meta, and para coupling constants were observed.

Scheme I



- a, R = CH₃
 b, R = OCH₃
 c, R = CO₂CH₃
 d, R = Cl
 e, R = Br

tion involving *o*-quinone dioximes (OQD), obtained by reducing BFO's, with pyruvaldehyde⁹ (B) in which the nitrogen atom is a nucleophile. Thus, the same substituents would be expected to exert opposite effects on the nitrogen atom involved in the reaction. An electron releasing substituent would reduce the electrophilicity of the nitrogen atom in A while enhancing its nucleophilicity in B. Thus, a major isomer in reaction A, which is obtained pure only by repeated crystallization, would be expected to be a minor one in B. The minor isomer in reaction A becomes a major product in reaction B thus allowing its isolation in pure form. All transformations, except for the BFO condensa-

Table II
Percentages of 7:6 Isomers in the Hydroxamic Acid Methyl Esters (4)

R	BFO reaction A	OQD reaction B
CH ₃	71:29	35:65
OCH ₃	83:17	20:80
CO ₂ CH ₃	20:80	82:18

tion reactions (A), have yields ranging from 85 to 90%, minimizing chances of loss of minor isomers.

The quinoxaline 1,4-dioxides were prepared following earlier procedures in moderate yields.¹⁰ Careful column chromatography of the mother liquors allowed the isolation of all the products formed with overall yields of 50–60%.¹¹

A summary of the nmr data used in calculating the various isomer percentages is presented in Table I. The chemical shifts of the aromatic protons in two pure isomers were first determined. Nmr spectra of mixtures of isomers from reactions A and B were then obtained.

Differences in the chemical shifts of the H-5 nuclei, which are doublets with meta coupling constants in one case and ortho in the other, allow the detection of the minor isomer. Its percentage is calculated directly from the integration spectrum as compared to the remainder of the aromatic region. That we are dealing with isomeric mixtures rather than impurities is evidenced by the correct elemental analyses obtained on the compounds whose nmr spectra were used for the calculations.

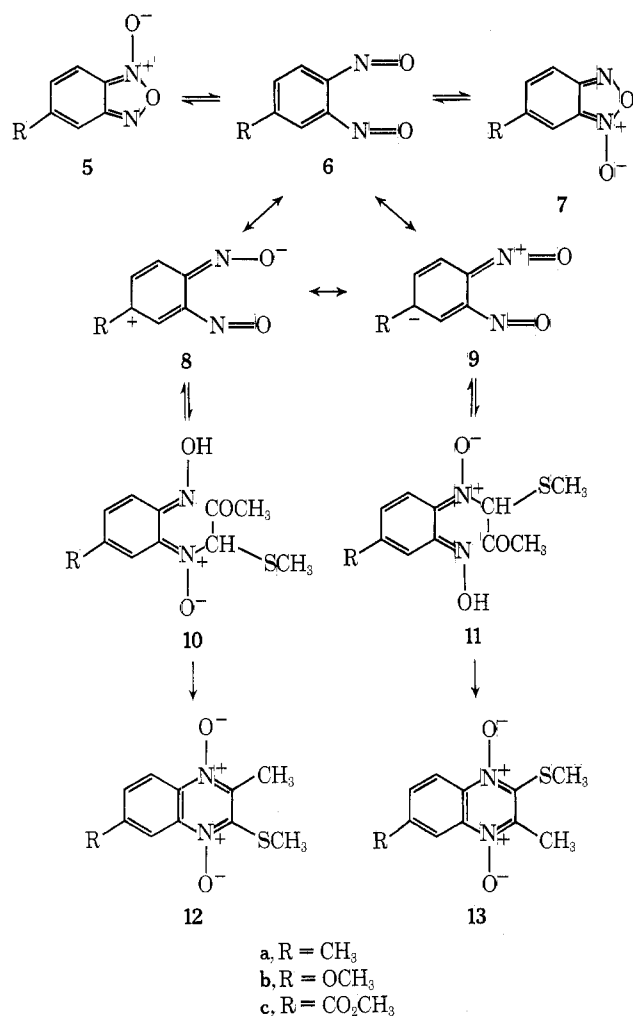
The percentages of 7:6 isomers in the hydroxamic acid methyl esters (4) are shown in Table II. As was predicted earlier, a major isomer in reaction A became the minor one in reaction B.

The experimental results on 5(6)-methoxy-BFO (Table I) confirm the earlier work of Haddadin and coworkers on the formation of isomerides.⁶ However, they are in partial agreement with the findings of Mason and Tennant⁷ and Duerckheimer⁸ in that the major isomer observed corresponds to the *only* product they isolated.

These results are best rationalized by assuming that BFO reacts in its *o*-dinitrosobenzene form. Intermediacy of this compound has been proposed in the rapid interconversions of BFO between forms 5 and 7.¹²

It can be seen from Scheme II that an electron-releasing substituent would stabilize the resonance form 8 over 9, while an electron-accepting substituent would have the

Scheme II



opposite effect. Accordingly, the meta nitroso group would suffer initial nucleophilic attack in the former case while the para nitroso group would be more reactive in the latter. Thus 5(6)-methoxy- and 5(6)-methyl-BFO would be expected to furnish the 7-substituted compounds (12a and 12b) as the major isomers while 5(6)-carbomethoxy-BFO leads preferentially to the 6-isomer 13c. This is in full agreement with the experimental results.

An earlier proposal⁷ suggested initial attack at N-3 in the most stable form of BFO, which is 5 for 5(6)-methoxy-BFO and 7 for 5(6)-carbomethoxy BFO,¹³ to rationalize the formation of certain isomers. Although such a mechanism explains the results obtained from the reactions of 5(6)-methoxy- and 5(6)-carbomethoxy-BFO, it does not accommodate the data on the 5(6)-methyl compound. A 50:50 mixture of 6- and 7-methylquinoxaline 1,4-dioxide isomers would be expected from the latter BFO since the tautomeric forms 5 and 7 were found to be of equal stability.

Earlier attempts to trap *o*-dinitrosobenzene have not been successful.¹⁴ The present work offers a significant experimental finding to establish the intermediacy of 6 in the rapid equilibrations of benzofuraxans. Similar arguments can be used to explain the results from the OQD reaction with pyruvaldehyde where in each case the opposite isomer to that obtained from the BFO reaction is expected and does predominate.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The nmr spectra were re-

corded on a Varian A-60 spectrometer. Microanalyses were performed by Micro-Analysis, Inc., Marshallton, Del.

General Method for the Preparation of Quinoxaline 1,4-Dioxides. Nearly equimolar quantities of BFO and acetyl methyl sulfide were dissolved in methanol, ammonia gas was bubbled in for a few minutes, and the reaction mixture was allowed to stand at room temperature overnight. The crystalline product was filtered off and washed with methanol and dried. Individual compounds follow.

3,6(7)-Dimethyl-2-methylthioquinoxaline 1,4-Dioxide (2a). 5(6)-Methyl-BFO (1a) (4.0 g, 26.7 mmol) and acetyl methyl sulfide (2.4 g, 23.1 mmol) were dissolved in methanol (100 ml). The product isolated weighed 1.1 g. Evaporation of the mother liquor gave a residue (5.0 g) which was chromatographed on silica gel (150 g). Eluting with chloroform (700 ml) gave an additional amount of the product (1.5 g) bringing the yields up to 45%. Recrystallization from methanol gave the analytical sample: mp 175–177°; nmr (CDCl₃) δ 2.6 (s, 3), 2.7 (s, 3), 2.9 (s, 3), 7.6 (q, 1, *J* = 2 and 9 Hz), 8.3 (d, 1, *J* = 2 Hz), 8.9 (d, 1, *J* = 9 Hz).

Anal. Calcd for C₁₁H₁₂N₂O₂S: C, 55.92; H, 5.11; N, 11.85. Found: C, 56.04; H, 4.92; N, 11.71.

Further elution of the column with 15% methanol in chloroform (600 ml) furnished 3,6(7)-dimethyl-1-hydroxy-2-iminoquinoxaline 4-oxide (0.22 g), mp 239–240°. The analytical sample was obtained from water.

Anal. Calcd for C₁₀H₁₁N₃O₂: C, 58.74; H, 5.37; N, 20.37. Found: C, 58.67; H, 5.38; N, 20.48.

6(7)-Methoxy-3-methyl-2-methylthioquinoxaline 1,4-Dioxide (2b). 5(6)-Methoxy-BFO (1b) (1.3 g, 7.9 mmol) and acetyl methyl sulfide (1.0 g, 9.6 mmol) were dissolved in methanol (20 ml). The product obtained after column chromatography (as above) weighed 1.35 g (68%). The analytical sample was obtained from methanol: mp 140–141°; nmr (CDCl₃) δ 2.7 (s, 3), 2.9 (s, 3), 4.0 (s, 3), 7.3 (q, 1, *J* = 3 and 9 Hz), 7.9 (d, 1, *J* = 3 Hz), 8.5 (d, 1, *J* = 9 Hz).

Anal. Calcd for C₁₁H₁₂N₂O₃S: C, 52.38; H, 4.76; N, 11.11. Found: C, 52.02; H, 4.83; N, 11.11.

The corresponding ammonolysis product 1-hydroxy-2-imino-6(7)-methoxy-3-methylquinoxaline 4-oxide was similarly obtained, mp 253–255°.

Anal. Calcd for C₁₀H₁₁N₃O₃: C, 54.29; H, 4.97; N, 19.00. Found: C, 54.51; H, 5.23; N, 18.79.

Methyl-3-methyl-2-methylthioquinoxaline-6(7)-carboxylate 1,4-Dioxide (2c). 5(6)-Carbomethoxy-BFO (1c) (5.0 g, 27 mmol) and acetyl methyl sulfide (2.7 g, 27 mmol) were dissolved in methanol (100 ml); the product weighed 1.9 g (44% based on recovered BFO of 2.0 g). The analytical sample was obtained from methanol–chloroform: mp 181–183°; nmr (CDCl₃) δ 2.8 (s, 3), 2.9 (s, 3), 4.1 (s, 3), 8.4 (q, 1, *J* = 1 and 8 Hz), 8.7 (q, 1, *J* = 2 and 8 Hz), 9.2 (br s, 1).

Anal. Calcd for C₁₂H₁₂N₂O₄S: C, 51.41; H, 4.28; N, 10.00. Found: C, 51.24; H, 4.06; N, 9.80.

3,6-Dimethyl- and 3,7-Dimethyl-1-hydroxyquinoxalin-2-one 4-Oxides (3a). Method A. A suspension of 2a (1.1 g, 4.58 mmol) in 3% aqueous potassium hydroxide (60 ml) was heated on a steam bath until a solution formed. This was cooled and neutralized with concentrated hydrochloric acid. The precipitate formed weighed 0.65 g (70%). Crystallization from trifluoroacetic acid furnished the analytical sample, mp 228–230°.

Anal. Calcd for C₁₀H₁₀N₂O₃: C, 58.26; H, 4.89; N, 13.58. Found: C, 57.95; H, 5.07; N, 13.35.

Method B. To a suspension of 5a (1.1 g, 7.5 mmol) in water (35 ml) was added 40% pyruvaldehyde (3 ml, 7.5 mmol). The red suspension was warmed up on a steam bath until the color changed to yellow. Upon cooling a precipitate formed (1.4 g). The analytical sample was obtained from trifluoroacetic acid, mp 228–232°.

Anal. Calcd for C₁₀H₁₀N₂O₃: C, 58.26; H, 4.89; N, 13.58. Found: C, 58.25; H, 5.04; N, 13.32.

1-Hydroxy-6-methoxy- and 1-Hydroxy-7-methoxy-3-methylquinoxalin-2-one 4-Oxides (3b). Method A. The procedure used for the preparation of 3a was followed to convert 2b (2.1 g, 8.4 mmol) to the product (1.7 g, 92%). The analytical sample was obtained from trifluoroacetic acid–methanol, mp 210–212°.

Anal. Calcd for C₁₀H₁₀N₂O₄: C, 54.06; H, 4.54; N, 12.61. Found: C, 53.99; H, 4.55; N, 12.48.

Method B. An identical procedure with that mentioned above was applied to 5b (0.85 g, 5 mmol) and pyruvaldehyde (2 ml of 40% solution) to furnish the product (0.8 g, 80%), mp 252–255°.

Anal. Calcd for C₁₀H₁₀N₂O₄: C, 54.06; H, 4.54; N, 12.61. Found: C, 53.78; H, 4.48; N, 12.74.

1-Hydroxy-3-methylquinoxalin-2-one-6- and -7-carboxylic Acid 4-Oxides (3, R = CO₂H). Compound **2c** (0.8 g, 3 mmol) was suspended in a mixture of methanol (5 ml) and 1 *N* potassium hydroxide (50 ml) and was heated on a steam bath for 0.5 hr. The cooled solution was acidified with 6 *N* hydrochloric acid. The precipitate formed (0.6 g (80%)) was crystallized from trifluoroacetic acid-methanol, mp above 280°.

Anal. Calcd for C₁₀H₈N₂O₅: C, 50.85; H, 3.39; N, 11.86. Found: C, 50.61; H, 3.67; N, 11.56.

Methyl-1-hydroxy-3-methylquinoxalin-2-one-6- and -7-carboxylate 4-Oxides (3c). The dioxime **5c** (0.96 g, 4.9 mmol) was suspended in water (30 ml) and heated on a steam bath. Pyruvaldehyde solution (40%) (1.5 ml) was added to the hot solution and the reaction mixture was allowed to cool down to room temperature. A crystalline precipitate formed (0.84 g, 70%). The analytical sample was obtained by crystallization from trifluoroacetic acid-methanol, mp 235°.

Anal. Calcd for C₁₁H₁₀N₂O₅: C, 52.80; H, 4.00; N, 11.20. Found: C, 53.09; H, 4.05; N, 11.28.

3,6-Dimethyl-1-methoxyquinoxalin-2-one 4-Oxide (4a). Crude **3a** (0.9 g, 4.4 mmol), obtained *via* method B was added to previously purified dimethyl sulfate (0.6 ml, 6.2 mmol) dissolved in dry acetone (250 ml). Potassium carbonate (0.75 g) was added and the reaction mixture was refluxed overnight. Acetone was evaporated and the residue was partitioned between chloroform and aqueous potassium carbonate. The organic layer was dried over magnesium sulfate, filtered, and evaporated to dryness to yield a residue (0.74 g). This was crystallized once from chloroform-ether to give the analytical sample, mp 146–148°. The nmr spectrum of this material showed the predominance of the 6-methyl over the 7-methyl isomer.

Anal. Calcd for C₁₁H₁₂N₂O₃: C, 60.21; H, 5.46; N, 12.65. Found: C, 60.19; H, 5.56; N, 12.84.

The pure 6 isomer was obtained after three crystallizations, mp 171–173°.

Anal. Calcd for C₁₁H₁₂N₂O₃: C, 60.21; H, 5.46; N, 12.65. Found: C, 60.09; H, 5.45; N, 12.93.

3,7-Dimethyl-1-methoxyquinoxalin-2-one 4-Oxide (4a). Crude **3a** (0.65 g, 3.2 mmol), obtained *via* method A, was esterified in the same manner to give a product (0.6 g, 80%). Crystallization from chloroform-ether gave the analytical sample whose nmr showed the predominance of the 7-methyl over the 6-methyl isomer, mp 149–154°.

Anal. Calcd for C₁₁H₁₂N₂O₃: C, 60.21; H, 5.46; N, 12.65. Found: C, 60.12; H, 5.37; N, 12.76.

The pure 7 isomer was obtained after three crystallizations, mp 186–188°.

Anal. Calcd for C₁₁H₁₂N₂O₃: C, 60.21; H, 5.46; N, 12.65. Found: C, 60.09; H, 5.88; N, 12.47.

1,6-Dimethoxy-3-methylquinoxalin-2-one 4-Oxide (4b). Crude **3b** (1.1 g, 4.9 mmol), obtained *via* method B, was esterified with excess diazomethane in ether. The suspension was allowed to stir at room temperature until all the compound went into solution. Excess diazomethane was decomposed with acetic acid followed by evaporation of the solution to dryness. The residue obtained was crystallized once from chloroform-ether (1.0 g, 94%), mp 160°. The nmr spectrum showed the predominance of the 6-methoxy over the 7-methoxy isomer.

Anal. Calcd for C₁₁H₁₂N₂O₄: C, 55.92; H, 5.12; N, 11.86. Found: C, 55.87; H, 5.04; N, 11.58.

The pure 6-methoxy isomer was obtained after three crystallizations, mp 183–185°.

Anal. Calcd for C₁₁H₁₂N₂O₄: C, 55.92; H, 5.12; N, 11.86. Found: C, 56.07; H, 5.32; N, 11.63.

1,7-Dimethoxy-3-methylquinoxalin-2-one 4-Oxide (4b). Crude **3b** (1.1 g, 4.9 mmol), obtained *via* method A, was esterified with diazomethane in ether. Usual work-up gave the product (0.92 g, 82%). Crystallization from chloroform-ether gave an analytical sample, mp 180–185°. The nmr spectrum showed the predominance of the 7-methoxy over the 6-methoxy isomer.

Anal. Calcd for C₁₁H₁₂N₂O₄: C, 55.92; H, 5.12; N, 11.86. Found: C, 56.02; H, 5.19; N, 11.56.

The pure 7-methoxy isomer was obtained after three crystallizations, mp 191–193°.

Anal. Calcd for C₁₁H₁₂N₂O₄: C, 55.92; H, 5.12; N, 11.86. Found: C, 56.16; H, 5.11; N, 11.51.

Methyl-1-methoxy-3-methylquinoxalin-2-one-6-carboxylate 4-Oxide (4c). Crude **3** (R = CO₂H) (0.5 g, 1.7 mmol), obtained *via* method A, was treated with excess diazomethane in ether until complete solution occurred. The usual work-up gave the product

(0.55 g). One crystallization from chloroform-ether gave the analytical sample, mp 207–209°. The nmr spectrum showed the predominance of the 6- over the 7-carbomethoxy isomer.

Anal. Calcd for C₁₂H₁₂N₂O₅: C, 54.50; H, 4.54; N, 10.60. Found: C, 54.44; H, 4.40; N, 10.40.

The nmr of the pure 6-carbomethoxy isomer was obtained by one further crystallization, mp 210–211°.

Anal. Calcd for C₁₂H₁₂N₂O₅: C, 54.50; H, 4.54; N, 10.60. Found: C, 54.77; H, 4.64; N, 10.36.

Methyl-1-methoxy-3-methylquinoxalin-2-one-7-carboxylate 4-Oxide (4c). Crude **3c** (0.6 g, 2.4 mmol) obtained *via* method B was esterified with diazomethane to give the product (0.66 g). One crystallization from chloroform-ether gave the analytical sample, mp 175–178°. The nmr spectrum showed the predominance of the 7- over the 6-carbomethoxy isomer.

Anal. Calcd for C₁₂H₁₂N₂O₅: C, 54.50; H, 4.54; N, 10.60. Found: C, 54.29; H, 4.54; N, 10.53.

The nmr spectrum of the pure 7-carbomethoxy isomer was obtained by repeated crystallization, mp 179–181°.

Anal. Calcd for C₁₂H₁₂N₂O₅: C, 54.50; H, 4.54; N, 10.60. Found: C, 54.33; H, 4.41; N, 10.46.

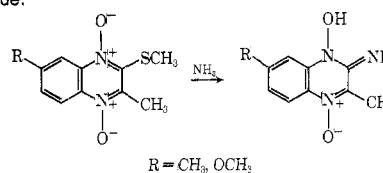
Methyl-*o*-benzoquinone Dioxime 4-carboxylate (5c). 5-Carbomethoxy-BFO (**1c**) (1.0 g, 5 mmol) and di-2,5-*tert*-butylhydroquinone (1.05 g, 5 mmol) were dissolved in tetrahydrofuran (30 ml), and ammonia gas was bubbled in for a few minutes. After standing at room temperature overnight, a dark crystalline precipitate was formed. The tetrahydrofuran solution was decanted. The residue was dissolved in water (20 ml) and filtered. Acidification of filtrate with dilute sulfuric acid precipitated the product, mp 134–135° (0.6 g).

Anal. Calcd for C₈H₈O₄N₂: C, 49.00; H, 4.08; N, 14.28. Found: C, 49.09; H, 4.13; N, 14.41.

Registry No.—**1a**, 5 isomer, 19164-41-1; **1a**, 6 isomer, 3524-05-8; **1b**, 5 isomer, 7791-49-3; **1b**, 6 isomer, 3524-06-9; **1c**, 5 isomer, 36389-06-7; **1c**, 6 isomer, 53178-59-9; **2a**, 6 isomer, 53209-82-8; **2a**, 7 isomer, 53209-85-1; **2b**, 6 isomer, 53209-83-9; **2b**, 7 isomer, 53209-86-2; **2c**, 6 isomer, 53209-84-0; **2c**, 7 isomer, 53209-87-3; **3a**, 6 isomer, 53178-64-6; **3a**, 7 isomer, 53178-60-2; **3b**, 6 isomer, 53178-65-7; **3b**, 7 isomer, 53209-90-8; **3c**, 6 isomer, 53178-66-8; **3c**, 7 isomer, 53178-61-3; **3** (R = CO₂H), 6 isomer, 53178-67-9; **3** (R = CO₂H), 7 isomer, 53209-89-5; **4a** 6-isomer, 53178-68-0; **4a**, 7 isomer, 53209-88-4; **4b**, 6 isomer, 53178-69-1; **4b**, 7 isomer, 53178-62-4; **4c**, 6 isomer, 53178-70-4; **4c**, 7 isomer, 53178-63-5; **5a**, 53178-71-5; **5b**, 53178-72-6; **5c**, 53178-73-7; acetyl methyl sulfide, 14109-72-9; 3,6-dimethyl-1-hydroxy-2-iminoquinoxaline 4-oxide, 53178-74-8; 3,7-dimethyl-1-hydroxy-2-iminoquinoxaline 4-oxide, 53178-75-9; 1-hydroxy-2-imino-6-methoxy-3-methylquinoxaline 4-oxide, 53198-71-3; 1-hydroxy-2-imino-7-methoxy-3-methylquinoxaline 4-oxide, 53198-72-4; pyruvaldehyde, 78-98-8; 2,5-di-*tert*-butylhydroquinone, 88-58-4.

References and Notes

- (1) (a) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 27, 1973. (b) Taken in part from the M.Sc. Thesis of N.D.A., University of Rhode Island, 1974.
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- (11) In addition to the starting BFO and quinoxaline 1,4-dioxides, a polar compound was isolated which proved to be an imino derivative, which was shown to be formed by ammonolysis of the parent quinoxaline 1,4-dioxide.



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- (14) See F. B. Mallory and C. S. Wood, *J. Org. Chem.*, **27**, 4109 (1962), for pertinent references.