the mixture deposited 11.96 g of phthalic acid and an additional 0.52 g was obtained on concentration of the filtrate. The final concentrate, 32 g of an oil, was dissolved in 600 ml of water and the solution was filtered clear, buffered with 150 ml of 10% sodium acetate solution to a pH of 5.5, washed with 100 ml of ethyl acetate, and then treated with a solution of 64.0 g of sodium tetraphenylboronate in 800 ml of water. A gummy precipitate was formed which was filtered, washed with water, air-dried, and then further washed with ether. The colorless tetraphenylboronate weighed 12.4 g, mp 113–115° dec, λ_{max}^{KBr} 1750, 1700 sh.

Anal. Calcd for $C_{31}H_{31}NO_3B$: C, 78.2; H, 6.6; N, 2.9. Found: C, 77.8; H, 6.9; N, 3.0.

The above tetraphenylboronate (12.00 g) was dissolved in a mixture of 400 ml of 95% ethanol and 100 ml of acetone and treated with a solution of 3.46 g of cesium chloride in 400 ml of 87% aqueous alcohol. The cesium tetraphenylboronate precipitate (9.0 g) as well as the additional solids (2.1 g) formed on concentration of the mixture were removed by filtration. Final evaporation to dryness resulted in 3.82 g of a colorless foam which, on crystallization with methanol–ether, yielded 3.20 g of the pure β-(β′-aminopropyl)-α-tetronic acid hydrochloride: mp 176–179° dec; $FeCl_3$ reaction purple; λ_{max}^{KBr} 1750, 1705; λ_{max}^{EtOH} 231.5 mμ (ε 9340).

Anal. Calcd for $C_7H_{11}NO_3 \cdot HCl$: C, 43.4; H, 6.2; N, 7.2; O, 24.5; Cl, 18.3. Found: C, 43.7; H, 6.4; N, 6.9; O, 24.4; Cl, 18.4.

Registry No.—Ethyl α-ethoxalyl-γ-phthalimidobutyrate, 25739-35-9; β-(β′-aminoethyl)-α-tetronic acid hydrochloride, 25739-36-0; ethyl α-methylene-γ-phthalimidobutyrate, 24249-90-9; ethyl γ-phthalimidovalerate, 10264-78-5; ethyl α-ethoxalyl-γ-phthalimidovalerate, 25739-39-3; β-(β′-aminopropyl)-α-tetronic acid tetraphenylboronate complex, 25776-64-1; β-(β′-aminopropyl)-α-tetronic acid hydrochloride, 25739-40-6.

One-Step Synthesis of Quinoxaline 1,4-Dioxides and Related Compounds

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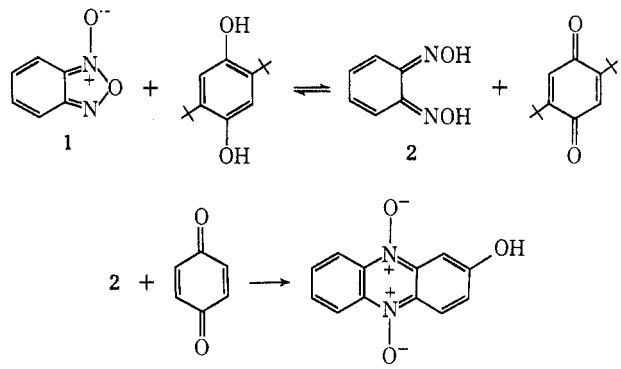
An elegant one-step synthesis of quinoxaline 1,4-dioxides, which comprised the reaction of benzofurazan 1-oxide (1) (BFO) with enamines or enolate anions, was reported in 1965.[2,3] With this method, a wide variety of quinoxaline 1,4-dioxides were prepared in good yields. α-Diketones, *e.g.*, biacetyl, did not react in the expected manner, and under a variety of conditions no 2-acetylquinoxaline 1,4-dioxide was isolated.[4] In the present work a probable explanation is offered for this failure which resulted in the discovery of a new method for the preparation of 1-hydroxyquinoxalin-2-one 4-oxides and quinoxaline 1,4-dioxides.

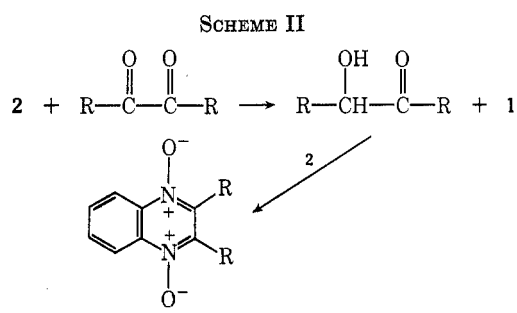
Studies in our laboratories have shown that *o*-quinone dioxime (2) was produced when BFO oxidized 2,5-di-*tert*-butyl hydroquinone to the corresponding *p*-quinone. This dioxime reacted with *p*-benzoquinone under neutral conditions to give 2-phenazinol 5,10-dioxide[5] (Scheme I).

SCHEME I



This discovery prompted us to investigate the reaction of biacetyl with *o*-quinone dioxime, two compounds of higher and lower oxidation states than the reactants used in the reactions of BFO mentioned earlier. The product isolated, 2,3-dimethylquinoxaline 1,4-dioxide, was of a lower oxidation state than expected had the two reactants simply combined. It was therefore assumed that an initial oxidation–reduction reaction took place in which the dioxime was oxidized to BFO[6] with simultaneous formation of α-hydroxy ketone, which then reacted with another molecule of *o*-quinone dioxime to give the observed products (Scheme II). Support for

SCHEME II



the above assumption was provided by the formation of BFO in this reaction. Furthermore when α-hydroxy ketones were substituted for α diketones, quinoxaline 1,4-dioxides were obtained. The reactions carried out are outlined in Table I.

A possible mechanism for the reactions of α-hydroxy ketones and α-hydroxy aldehydes with the dioxime is outlined in Scheme III. Even though ionic intermediates are presented, a radical ionic pathway cannot be excluded at this time.

Extension of this reaction to α-ketoaldehydes resulted in the formation of hydroxamic acids, **8a** and **8b**, in 50–60% yields (Scheme IV). A similar mechanism accounts for the formation of these products without invoking an initial oxidation–reduction reaction.

This synthetic method is not superior to present methods for the preparation of quinoxaline 1,4-dioxides. However, it represents a major improvement over ear-

(1) Department of Pharmaceutical Chemistry, College of Pharmacy, University of Rhode Island, Kingston, R. I. 02881.

(2) M. J. Haddadin and C. H. Issidorides, *Tetrahedron Lett.*, 3253 (1965).

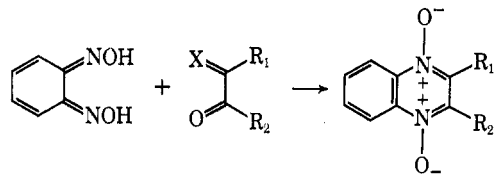
(3) M. J. Haddadin and C. H. Issidorides, *J. Org. Chem.*, **31**, 4067 (1966).

(4) J. D. Johnston, unpublished results.

(5) B. W. Dominy, unpublished work.

(6) *o*-Quinone dioxime has been oxided to benzofurazan 1-oxide: T. Zincke and P. Schwarz, *Justus Liebigs Ann. Chem.*, **307**, 39 (1899).

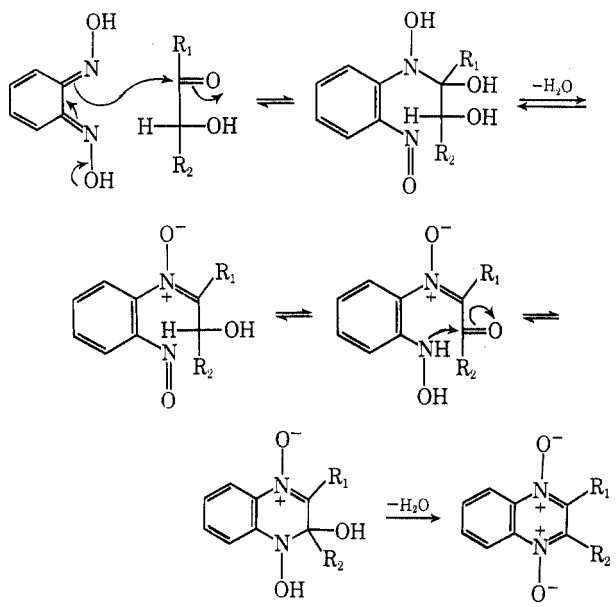
TABLE I



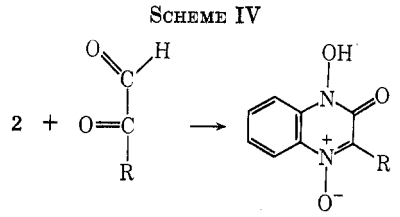
Compd no.	R_1	R_2	X	Mp, °C	% yield	Ref
3	CH_3	CH_3	O	181–183	16	*a*
4	CH_2CH_2–	CH_2CH_2	O	170–172	7	*b*
5	CH_3	H	H, OH	178–179	14	*b*
6	H	H	H, OH	227–229	5	*b*
7	CH_2OH	H	H, OH	198–199	16	

[a] British Patent 668,412 (1958). [b] H. McIlwain, *J. Chem. Soc.*, 322 (1943).

SCHEME III



SCHEME IV



8a, R = H
b, R = CH_3

lier routes for the synthesis of 1-hydroxyquinoxalin-2-one 4-oxides.[7]

Experimental Section

General Procedure for Quinoxaline 1,4-Dioxides (3–7).—A mixture of equimolar quantities of *o*-quinone dioxime and the carbonyl compound was dissolved in tetrahydrofuran (0.01 mol/30 ml) and refluxed for few hours. The solvent was then evaporated and the residue chromatographed on acid-washed Florisil, eluting first with benzene and then with chloroform. The $CHCl_3$ eluates were crystallized from methanol or a mixture of methanol–chloroform. The compounds isolated had identical physical data to authentic samples.

1-Hydroxyquinoxalin-2-one 4-Oxide (8a).—*o*-Quinone dioxime (6.9 g, 0.05 mol) was suspended in water (50 ml) and glyoxal (20 ml of 30% aqueous solution) was added. The suspension was heated on the steam bath for 5 min and a precipitate formed (6.0 g) (65%). This crystallized from methanol had mp 255–257°. The nmr spectrum had the following chemical shifts: δ 7.3–7.9 (3 H, m); 8.1 (1 H, s); 8.26 (1 H, q, $J_{5,6}$ = 8 Hz, $J_{5,7}$ = 2 Hz); 11.6 (1 H, broad multiplet, exchanges with D_2O). Ir (KBr) showed absorptions at 2.8, 6.2, and 7.5 μ; uv λ_{max}^{MeOH} 420 mμ (ϵ 470), 327 (470), 257 (2800), and 230 (1870).

Anal. Calcd for $C_8H_6O_3N_2$: C, 53.93; H, 3.37; N, 15.17. Found: C, 53.83; H, 3.37; N, 15.37.

3-Methyl-1-hydroxyquinoxalin-2-one 4-Oxide (8b).—Following the procedure for **8a** using methyl glyoxal, the product was formed in 50% yield, mp 231–232° (lit.[7] 216–217°). The physical data were similar to those of **8a**.

Anal. Calcd for $C_9H_8O_3N_2$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.77; H, 4.44; N, 14.44.

Registry No.—Biacetyl, 431-03-8; *o*-quinone dioxime, 14208-17-4; **7**, 20492-05-1; **8a**, 26438-47-1; **8b**, 26438-48-2.

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Substituent Effects on Hydrogen Bonding of Monosubstituted Phenols to Chloride Ion

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Recent publications[1,2] dealing with hydrogen bonding of chloride ion in nonpolar media prompted us to report some of our data on the interaction of monosubstituted phenols with chloride ion in methylene chloride.

Solutions of various phenols and benzyltriphenylphosphonium chloride (1:1 mol ratio) were prepared in anhydrous methylene chloride and the nmr chemical shifts of the hydroxyl protons were determined at 35°. The results are listed in Table I. A good linear correlation (see Figure 1) was obtained by plotting the chemical shift for the meta- and para-substituted phenols against σ values[3,4] (or σ^- values[3] in the special cases of

(1) G. G. Arzoumanidis, *Chem. Commun.*, 217 (1969).
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(3) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(4) M. T. Tribble and J. G. Traynham, *J. Amer. Chem. Soc.*, **91**, 379 (1969).