101–102°; ir (KBr) 3050 (w), 3035 (w), 3000 (w, aromatic), 2910 (w), 2865 (w, CH_2), 1600 (w), 1575 (w), 1489 (ms, aromatic), 1440 (ms), 1388 (ms, CH_2), 1245 (w), 1213 (w), 1160 (w), 1062 (w), 1027 (w, aromatic), 920 (w), 915 (w), 912 (w), 785 (ms), 780 (ms), 733 (ms), 718 (s), 686 (vs, aromatic); nmr ($CHCl_3$-*d*) δ 7.00 [s, 10.2, 4,5-(C_6H_5)], 3.33 (s, 3.8, 3,6-CH_2).

Anal. Calcd for $C_{16}H_{14}S_2$ (270.42): C, 71.07; H, 5.22. Found: C, 71.25; H, 5.29.

Further elution with ether gave an unidentified orange, pungent liquid (0.44 g) which was not identified.

6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin is quite unstable towards heat. On sublimation, in addition to the white solid (**7**) isolated above, a yellow crusty solid was obtained. This was found to be a mixture of the tetrasulfide **7**, the disulfide **6**, 3,4-diphenylthiophene (**8**), and sulfur. Similar decomposition took place when **7** was heated in refluxing xylene.

The nmr spectrum of the initially isolated crude material in the above reaction showed the presence of all the compounds isolated above. Because of the clear separation of signals for methylenic protons in the tetrasulfide **7** from those in the disulfide **6**, calculation of the molar ratio of the three products was possible. The molar ratio tetrasulfide–disulfide–2,3-diphenylthiophene was calculated to be 1:1.6:3.5. This was almost identical with the ratio of the isolated products.

Reactions of *cis*- and *trans*-1,4-dibromo-1,4-diphenyl-2-butene with sodium polysulfide (Table I) were run using the conditions and method of analysis described above.

6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-Oxide (**9**).—6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (**7**) (0.91 g, 2.72 mmol) was dissolved in methylene chloride (36 ml) and cooled to −25 to −30°. A solution of *m*-chloroperbenzoic acid (0.55 g, 2.72 mmol) in 21 ml of methylene chloride was also cooled to −25 to −30° and was added drop by drop to the above solution with stirring over a period of 30 min. The resulting mixture was allowed to warm slowly to room temperature (1 hr) and gave a yellow solution. This was washed with 5% sodium bicarbonate solution (2 × 50 ml) and water (1 × 50 ml) and was dried overnight (Drierite). Evaporation of the methylene chloride solution gave a pale yellow solid, which on crystallization from carbon tetrachloride–hexane gave 0.34 g (0.96 mmol, 35%) of 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-oxide (**9**): mp 135.3–137.3°; ir (KBr) 1060 cm^{-1} (S=O); nmr ($CHCl_3$-*d*) two overlapping AB quartets: ν_A 4.94, ν_B 3.62, J_{AB} = 14.3; $\nu_{A'}$ 5.32, $\nu_{B'}$ 4.49, $J_{A'B'}$ = 12.8; 7.13 (C_6H_5).

Anal. Calcd for $C_{16}H_{14}OS_4$ (350.54): C, 54.82; H, 4.02. Found: C, 54.80; H, 4.05.

Registry No.—**2**, 2548-47-2; **3**, 34826-14-7; **4**, 34804-71-2; **5**, 6363-17-3; **6**, 34804-73-4; **7**, 34804-74-5; **8**, 16939-13-2; **9**, 34804-76-7; **10**, 34804-77-8; **11**, 34792-39-7; disulfur monoxide, 20901-21-7; *meso*-2,3-diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 22985-90-6; *meso*-2,3-di-2-naphthyl-2,3-butanediol, 24227-54-1; *dl*-2,3-di-2-naphthyl-2,3-butanediol, 24227-55-2; 1,4-dibromo-2,3-di-2-naphthyl-2-butene, 34804-80-3.

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Benzofurazan Oxide. Reaction with Sulfur Enolate Anions

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This paper reports a new synthesis of 2-substituted 1-hydroxy-3-oxobenzimidazoles, in fair yields, from the reaction of benzofurazan oxide and β-carbonyl sulfones. 2-Phenylthioacetophenone, however, gave the corresponding quinoxaline 1,4-dioxide.

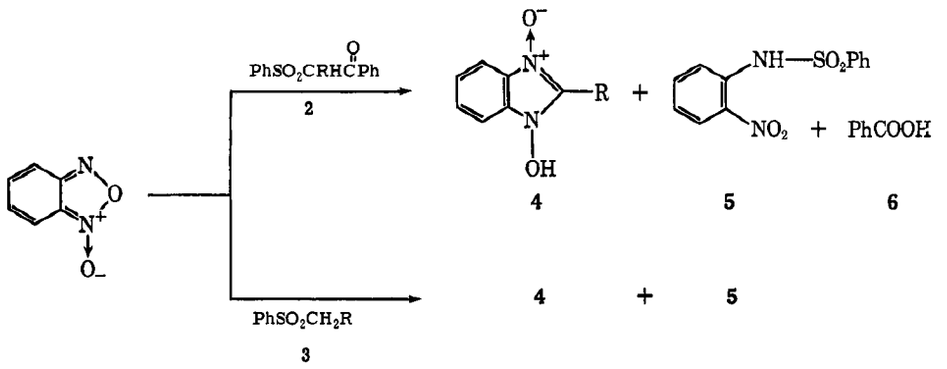
The condensation of benzofurazan oxide (**1**) with enamines[3] and other enolate anions[4,5] to give substituted quinoxaline 1,4-dioxides has been reported and a mechanism for the reaction has been suggested. The condensation of benzofurazan oxide with primary and secondary aliphatic nitro compounds[6] in basic media to yield 1-hydroxy-3-oxobenzimidazole and 1,3-dioxobenzimidazole derivatives, respectively, has also been reported. In this paper we report a new synthetic route to 1-hydroxy-3-oxobenzimidazole (**4R**$_1$) and its 2-substituted derivatives from the reaction of β-keto sulfones **2** and α-sulfonyl carboxamides **3** with benzofurazan oxide in an alkaline medium (Scheme I). On the other hand, 2-phenylthioacetophenone reacted with benzofurazan oxide to give a compound similar to those described by Haddadin, *et al.*,[4] which was assigned the quinoxaline 1,4-dioxide structure (Scheme II). (The compounds obtained by the reaction of benzofurazan oxide with substituted 2-phenylthioacetophenone will be the subject of a subsequent paper.)

Synthesis.—β-Keto sulfones **2** and α-sulfonyl carboxamides **3** were synthesized by the direct reaction of sodium benzenesulfinate dihydrate with the corresponding α-halo ketones and α-halo amides, respectively.[7] 2-Phenylthioacetophenone (**7**) was prepared from 2-bromoacetophenone and sodium thiophenate in a Williamson type synthesis. The structures of all the starting materials were confirmed by ir and nmr spectroscopy.

The reaction of 2-benzenesulfonylacetophenone (**2R**$_1$) with benzofurazan oxide in 4% methanolic potassium hydroxide solution afforded 1-hydroxy-3-oxobenzimidazole (**4R**$_1$) in 90% yield. 2-Nitrobenzenesulfonanilide (**5**) and benzoic acid (**6**) were the major byproducts that were isolated. The structure of **4R**$_1$ was established by its controlled reduction with carbon disulfide to 1-hydroxybenzimidazole (**11**), which is in tautomeric equilibrium with the 3-oxobenzimidazole **12**.[8] The melting point, ir, and nmr of **11** were identical with those of an authentic sample prepared by the reduction of *o*-nitroformanilide with ammonium sulfide.[9]

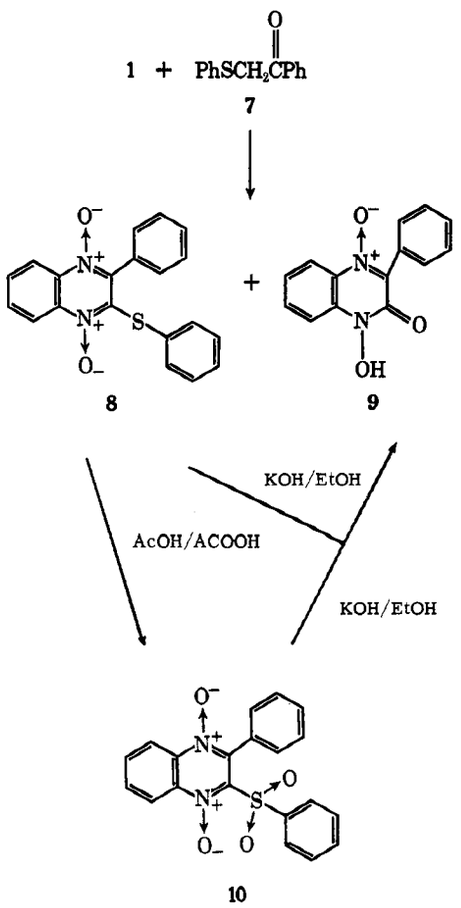
(1) Submitted in partial fulfillment of the doctoral degree requirements.
(2) Submitted in partial fulfillment toward the masters degree requirements.
(3) M. J. Haddadin and C. H. Issidoridis, *Tetrahedron Lett.*, 3253 (1965).
(4) M. J. Haddadin and C. H. Issidoridis, *J. Org. Chem.*, **31**, 4067 (1966).
(5) M. J. Haddadin, G. Agopian, and C. H. Issidorides, *ibid.*, **36**, 514 (1971).
(6) (a) J. D. Johnston, M. Abu El-Haj, B. W. Doming, J. W. McFarland, C. H. Issidorides, and M. J. Haddadin, IUPAC Meeting in London, July 1968, Abstract H 4, 437; (b) 156th National Meeting, of the American Chemical Society, Atlantic City, N. J., Sept 1968; (c) M. J. Abu El-Haj, *J. Org. Chem.*, in press.
(7) C. M. Suter, "The Organic Chemistry of Sulfur," Wiley, Chapman and Hall, London, 1944, pp 658–762.
(8) S. Takahashi and H. Kano, *Chem. Pharm. Bull.*, **11**, 1375 (1963).
(9) S. von Niementowski, *Ber.*, **20**, 1874 (1887).

SCHEME I



2, R_1 = H; R_2 = CH_3; R_3 = Et; R_4 = Bu
3, R_5 = O=CNH_2; R_6 = O=CNHPh; R_7 = O=$CN(Et)_2$; R_8 = O=CN (i-Pr)$_2$; R_9 = morpholino carbonyl; R_{10} = O=$CNCH_3Ph$; R_{11} = O=COEt

SCHEME II



Its reduction with Raney Ni in alkaline solution gave benzimidazole **14** (Scheme III). No 2-benzenesulfonyl-3-phenylquinoxaline 1,4-dioxide (**10**) or 1-hydroxy-3-phenylquinoxalin-2-one 4-oxide (**9**), the product expected to result from **10** under the reaction conditions, were isolated or observed by separating the product on a Florisil chromatographic column or with tlc, and testing by ir spectroscopy.

2-Alkyl-2-benzenesulfonylacetophenones reacted with benzofurazan oxide in the same way to give the 2-alkyl derivatives of 1-hydroxy-3-oxobenzimidazole $4R_2$, R_3, R_4 in low yields. The structure of 1-hydroxy-2-methyl-3-oxobenzimidazole ($4R_2$) was proved by its independent synthesis from o-quinone dioxime and acetaldehyde as previously reported by Katritzky[10] and his coworkers.

2-Benzenesulfonylacetamides $3R_5$–R_{10} reacted with benzofurazan oxide in basic media to give 1-hydroxy-3-oxobenzimidazole-2-carboxamides $4R_5$–R_{10}, respectively. o-Nitrobenzenesulfonanilide was the only by-product that was isolated. Structural assignment of these compounds was based on their nmr spectra, elemental analyses, and their analogous ir spectra to that of the parent molecule (Table I).

Ethyl 2-benzenesulfonylacetate reacted with benzofurazan oxide in 4% methanolic potassium hydroxide solution to give 1-hydroxy-3-oxobenzimidazole-2-carboxylic acid ($4R_{11}$), which was isolated as a mixture of the acid and its potassium salt. Furthermore, the acid hydrolysis of 1-hydroxy-3-oxobenzimidazole-2-carboxamide ($4R_5$) gave an acid which was identical with $4R_{11}$.

2-Phenylthioacetophenone (**7**) was found to react with benzofurazan oxide in 1% methanolic potassium hydroxide solution to give 2-phenylthio-3-phenylquinoxaline 1,4-dioxide (**8**) and 1-hydroxy-3-phenylquinoxaline-2-one 4-oxide (**9**) with o-quinone dioxime, phenyl disulfide, and benzenethiol as by-products. No 1-hydroxy-3-oxobenzimidazole ($4R_1$) was detected. Treating **8** with methanolic potassium hydroxide converted it slowly to **9** with the liberation of benzenethiol. Oxidation of **8** gave 2-benzenesulfonyl-3-phenylquinoxaline 1,4-dioxide (**10**). The sulfone **10** reacted immediately with potassium hydroxide to give **9**. The structure of **8** was established by its ir spectrum, which displayed bands at 1340 (N-oxide), 750 (ortho-substituted phenyl), and 695 cm^{-1} (monosubstituted phenyl). The nmr spectrum showed singlets at δ 7.07 (5 H) and 7.30 ppm (5 H) and two multiplets centered at δ 7.69 (2 H) and 8.40 ppm (2 H). The two hydrogens at δ 8.40 ppm are consistent with the expected deshielding effect on the protons at positions 5 and 8. The ir spectrum of **9** displayed bands at 3460 (hydroxyl), 1608 (carbonyl), 1350 (N-oxide), and 760 cm^{-1} (ortho-substituted phenyl). Its nmr spectrum showed a multiplet centered at δ 7.88 ppm (8 H) and a doublet at δ 8.40

(10) A. J. Boulton, A. C. Gripper Gray, and A. R. Katritzky, *J. Chem. Soc. B*, 911 (1967).

SCHEME III

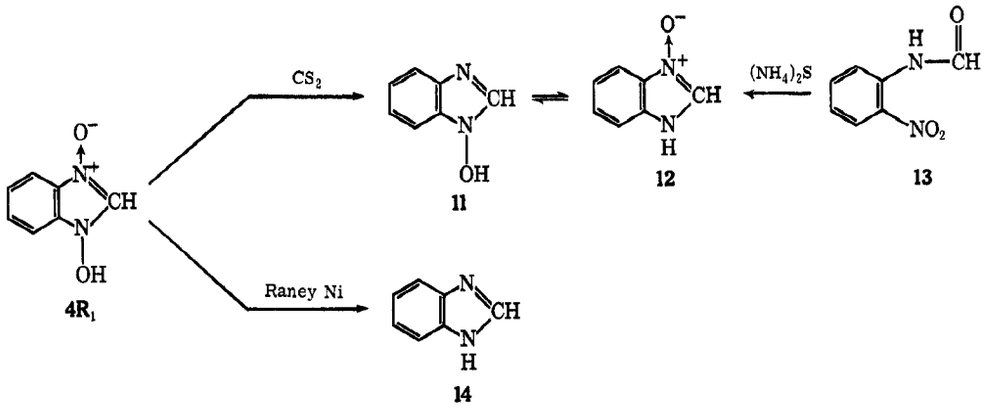


TABLE I

PHYSICAL CONSTANTS OF 1-HYDROXYBENZIMIDAZOLE 3-OXIDE DERIVATIVES (4)[a]

	R	Mp, °C	Yield, %	Nmr (CF3COOH), ppm		J, Hz	Ir, cm⁻¹
R_1	H	224 dec	90	m 7.72	4 H		3085, 1340, 1255, 1217, 1145, 1065, 745, 640
				s 9.23	1 H		
R_2	CH_3	200–201 dec	35	s 2.91	3 H		3100, 1350, 1300, 1225, 1170, 1100, 1050,
				m 7.69	4 H		970, 870, 760, 740
R_3	Et	190–191 dec	28	t 1.58	3 H	7	1350, 1290, 1210, 1150, 1052, 855, 750
				q 3.48	2 H	7	
				m 7.70	4 H		
R_4	Bu	172–174 dec	24	t 1.05	3 H	5.5	3100, 1360, 1300, 1250, 1150, 1108, 1050,
				m 1.3–2.17	4 H		840, 740
				t 3.48	3 H	7.5	
				m 7.70	4 H		
R_5	$O{=}CNH_2$	218–220 dec	12	m 7.82	4 H		3280, 3130, 1685, 1608, 1480, 1340, 1300,
				s 8.44	2 H		1215, 1165, 1100, 1015, 990, 860, 748,
							710, 680
R_6	O=CNHPh	218–219 dec	39	m 7.45	5 H		3270, 1687, 1605, 1561, 1352, 1320, 1302,
				m 7.82	4 H		1257, 1210, 1112, 1022, 1000, 878, 742,
				s 10.08	1 H		720, 690
R_7	$O{=}CN(Et)_2$	189–189.5 dec	57	t 1.41	3 H	7	3100, 1662, 1520, 1420, 1380, 1369, 1304,
				t 1.49	3 H	7	1269, 1212, 1150, 1135, 1117, 1099, 1073,
				q 3.60	2 H	7	877, 815, 745, 728
				q 3.88	2 H	7	
				m 7.82	4 H		
R_8	$O{=}CN(i\text{-}Pr)_2$	215–217 dec	51	d 1.4	6 H	6	3110, 1660, 1525, 1452, 1435, 1365, 1330,
				d 1.65	6 H	6	1310, 1252, 1212, 1160, 1140, 1065, 1050,
				m 3.39–4.29	2 H		881, 748, 720
				m 7.75	4 H		
R_9	morpholino carbonyl	200–202 dec	65	m 3.65–4.2	8 H		1670, 1520, 1365, 1300, 1275, 1245, 1190,
				m 7.81	4 H		1140, 1105, 1065, 1030, 845, 750
R_{10}	$O{=}CNCH_2Ph$	205–206 dec	50	s 3.77	3 H		1670, 1590, 1519, 1490, 1405, 1352, 1295,
				s 7.39	5 H		1278, 1140, 1108, 1075, 1035, 875, 775, 745
				m 7.71	4 H		
R_{11}	O=COH	>300 dec	40	m 7.75			3400, 1660, 1590, 1490, 1350, 1250, 1210,
							1150, 1085, 1000, 925, 875, 740

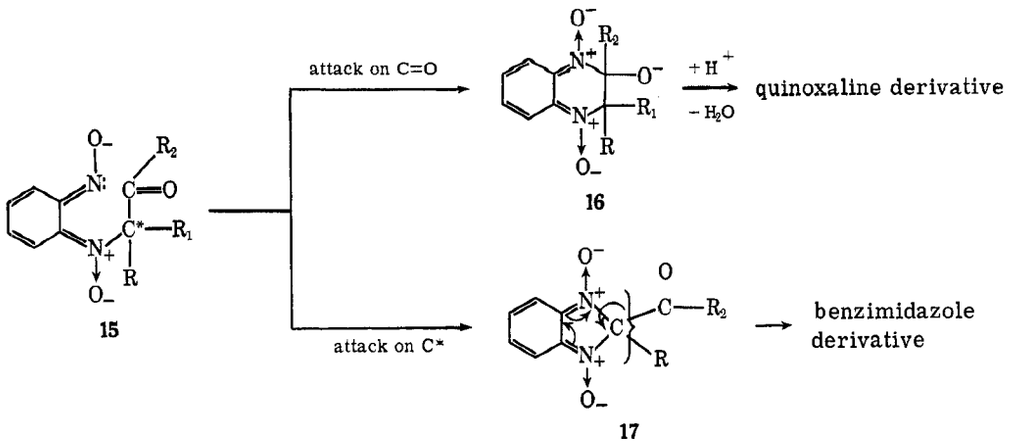
[a] Except for $4R_{11}$, which resisted recrystallization, the analyses of these compounds checked within 0.35%.

ppm (1 H, J = 8 Hz). In this case deshielding is reduced at position 8 and only the 5 proton absorbs downfield. The ir spectrum of **10** showed two bands at 1360 and 1340 cm^{-1} (N-oxide) in addition to the sulfone bands at 1318, 1165, and 1088 cm^{-1}. Further proof for the structural assignment of these compounds was based on their elemental analyses and on the fact that similar enolate anions gave the corresponding quinoxaline 1,4-dioxides.[2,3,4]

Under the reaction conditions none of the starting materials **2** or **3** were cleaved, thus eliminating the possibility of cleavage of either the sulfone or the carbonyl group in $2R_1$ as the initial step leading to product formation. Also, the synthesis of 1-hydroxy-2-phenyl-3-oxobenzimidazole failed due to the ease of cleavage of 2-phenyl-2-benzenesulfonylacetophenone to give phenyl benzyl sulfone and benzoic acid. This cleavage was also confirmed in the absence of benzofurazan oxide. Benzofurazan oxide is known to be readily reduced in alcoholic potassium hydroxide solution to give o-quinone dioxime;[11] however, o-quinone dioxime was also eliminated as a possible intermediate since it did

(11) D. L. Hammick, W. A. M. Edwardes, and E. R. Steimer, *J. Chem. Soc.*, 3308 (1931).

SCHEME IV



not react with 2-benzenesulfonylacetophenone under the reaction conditions. Benzofurazan oxide reacted when treated separately with sodium benzenesulfinate under the same reaction conditions to give *o*-nitrobenzenesulfoanilide (**5**) nearly quantitatively.

These data suggest that 1-hydroxy-3-oxobenzimidazole derivatives **4** and the substituted quinoxaline 1,4-dioxide **8** could have been formed through a mechanism involving an initial attack by the enolate anion on N_1, N_2, and/or on the dinitroso intermediate of the equilibrating benzofurazan oxide tautomers[12] to lead to intermediate **15**. It is not discernible at this time where the initial attack occurs or if different modes of attack result in different products. Once it is formed, intermediate **15** could cyclize by an internal condensation at the carbonyl carbon to lead through **16** to the quinoxaline derivative, and could also cyclize by a nucleophilic substitution at C* to lead through **17** to the benzimidazole derivative depending on the nature of R_1 (Scheme IV). A phenylsulfonyl group facilitates substitution because it is a better leaving group (pK_a of its corresponding acid is 1.84),[13] when compared with the thiophenoxide group (pK_a of its corresponding acid is 6.52).[14] Furthermore, the partial positive charge on the sulfur induces a positive charge on C*, thus making it more susceptible to nucleophilic attack. A similar case where the benzenesulfonyl group leaves very easily is the immediate reaction of 2-benzenesulfonyl-3-phenylquinoxaline 1,4-dioxide (**10**) with potassium hydroxide to give the corresponding ketone **9** and potassium sulfinate (Scheme II). A thiophenoxide or benzoyl group for R_1 makes substitution difficult in the first case and rather impossible in the latter case since neither one is a good leaving group. When a poor leaving group is present the attack is on the carbonyl carbon and the quinoxaline derivative forms. Once the five-membered ring **17** is formed, abstraction of the proton when R = H or cleavage of the ketone group when R = alkyl could lead directly to the product. Attempts to trap intermediate **17** by replacing R by a methyl and (COR_2) by a substituted amide failed and no reaction was observed between benzofurazan oxide and 2-benzenesulfonyl-*N*,*N*-diethylpropionamide.

(12) A. R. Katritzky and A. J. Boulton, "Advances in Heterocyclic Chemistry," Vol. 10, Academic Press, New York and London, 1969, p 5.

(13) R. K. Burkhard, D. E. Sellers, F. Decay, and J. L. Lambert, *J. Org. Chem.*, **24**, 768 (1959).

(14) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, and L. T. Ditsch, *J. Amer. Chem. Soc.*, **82**, 4899 (1960).

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and were uncorrected. Microanalyses were performed by M-H-W Laboratories. Infrared spectra were determined on a Perkin-Elmer Model 621 spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian Model HA-60 spectrometer. Chemical shifts are reported in units using tetramethylsilane as an internal reference.

General Procedure for the Reaction of Benzofurazan Oxide with β-Carbonyl Sulfones.—In an erlenmeyer flask were placed 0.02 mol of the β-carbonyl sulfone, 5.44 g (0.04 mol) of benzofurazan oxide, and 50 ml of methanol. The crystals were dissolved by warming and 50 ml of 8% methanolic KOH solution was added. The solution was left at room temperature for 12 hr and was filtered from any *o*-nitrobenzenesulfonanilide (potassium salt) that could have formed. The solvent was evaporated to dryness and 15 ml of water was added to the resulting black residue. Stirring and cooling crystallized another portion of *o*-nitrobenzenesulfonanilide (potassium salt). The mixture was filtered and the black aqueous filtrate was neutralized with concentrated HCl until a few droplets of oil formed. The oil was extracted with ether and the aqueous layer was separated and neutralized further with concentrated HCl to give an oily precipitate. The precipitate was triturated with acetone to give fairly pure crystals of the 1-hydroxy-3-oxobenzimidazole derivative. The products were all soluble in acidic and basic media and insoluble in acetone and were recrystallized from methanol, ethanol, and/or water.

A.—When 2-alkyl-2-benzenesulfonylacetophenones (**2**) were allowed to react, the reaction mixture was warmed to 40–60° for 8 hr, then worked up.

B.—The reaction mixture with 2-benzenesulfonylacetamide (**3**, R = $CONH_2$) was warmed for 30 min and was then worked up.

C.—The reaction mixture with ethyl 2-benzenesulfonylacetate was warmed to 50° for 3 hr and the resulting 1-hydroxy-3-oxobenzimidazole-2-carboxylic acid was recrystallized by dissolving it several times in 1% KOH solution and neutralizing with HCl.

Reaction of Benzofurazan Oxide with 2-Phenylthioacetophenone (7).—In an erlenmeyer flask were placed 6 g (0.027 mol) of **7**, 3.6 g (0.027 mol) of benzofurazan oxide, and 100 ml of 1% ethanolic KOH solution. The mixture was kept at room temperature by cooling and was then stirred for 45 min. The solution was cooled in an ice bath and the heavy precipitate that formed was collected and recrystallized from ethanol to give 2.9 g (29%) of yellow crystals of 2-phenylthio-3-phenylquinoxaline 1,4-dioxide (**8**): mp 205–207°; nmr ($DCCl_3$) 7.07 (s, 5 H), 7.30 (s, 5 H), 7.69 (m, 2 H), 8.40 ppm (m, 2 H); ir 1340, 1310, 1265, 1080, 1020, 910, 783, 750, 740, 695 cm^{-1}.

Anal. Calcd for $C_{20}H_{14}N_2O_2S$: C, 69.36; H, 4.05; N, 8.10; S, 9.24. Found: C, 69.50; H, 4.05; N, 7.96; S, 9.13.

The methanolic filtrate from above was evaporated and the black oily residue was dissolved in 35 ml of water and extracted with ether to rid it of phenyl disulfide. The aqueous layer was neutralized with concentrated HCl until an oily precipitate formed. Recrystallization from ethanol afforded 1.83 g (26%) of hairy needles of 1-hydroxy-3-phenylquinoxalin-2-one 4-oxide (9): mp 195–196°; nmr (DMSO) 7.88 (m, 8 H), 8.40 ppm (d, 1 H); ir 3460, 1608, 1590, 1350, 1315, 1250, 1225, 1080, 890, 850, 760, 690 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.94; N, 11.02. Found: C, 66.36; H, 3.88; N, 11.16.

Reaction of 2-Phenylthio-3-phenylquinoxaline 1,4-Dioxide (8) with Peroxyacetic Acid.—In an erlenmeyer flask were placed 1 g (0.003 mol) of **8** and 30 ml of acetic acid. The solution was warmed to dissolve all the crystals and 6 ml of peroxyacetic acid was introduced. The solution was left for 24 hr and the precipitate that formed was collected and recrystallized from methanol to give 0.4 g (35%) of yellow needles of **10**: mp 231–233°; nmr (CF_3COOH) 7.59 (m, 8 H), 8.40 (m, 4 H), 8.56 ppm (m, 2 H); ir 1360, 1340, 1318, 1270, 1165, 1088, 920, 780, 765, 730, 710, 690 cm^{-1}.

Anal. Calcd for $C_{20}H_{14}N_2O_4S$: C, 63.49; H, 3.57; N, 7.41; S, 8.47. Found: C, 63.40; H, 3.57; N, 7.28; S, 8.61.

Reaction of 1-Hydroxy-3-oxobenzimidazole ($4R_1$) with CS_2.—In an erlenmeyer flask was placed a mixture of 1.59 g (0.01 mol) of $4R_1$, 50 ml of methanol, and 8.6 g (0.1 mol) of CS_2 and the mixture was stirred vigorously until most of the crystals dissolved. The solution was filtered and the solvent was evaporated to dryness. The yellowish oily residue was freed of sulfur by triturating with CS_2. The oil that was left was recrystallized from ethanol to give 0.5 g (37%) of yellow crystals of 1-hydroxybenzimidazole (**11**): mp 210–212° (lit.[9] mp 210–212°); ir 3175, 1590, 1360, 1318, 1230, 1122, 1090, 990, 910, 840, 765, 750, 740, 720 cm^{-1}. Product **11** was identical (mixture melting point, superimposable ir spectra) with an authentic sample prepared by the reduction of o-nitroformanilide with ammonium sulfide.

Reaction of 1-Hydroxy-3-oxobenzimidazole ($4R_1$) with Raney Ni.—In a beaker were placed 1.5 g (0.01 mol) of $4R_1$ and 15 ml of 12% KOH solution. A total of 2 g of Raney Ni was introduced at several intervals of time while warming. The solution was filtered and was neutralized with concentrated HCl. The precipitate that formed was filtered and the neutral filtrate was extracted with ether. The precipitate was boiled with 75 ml of acetone and filtered. The ether extract and acetone filtrate were mixed and the solvent was evaporated. The resulting oil was recrystallized from water to give 0.15 g (13%) of benzimidazole **14**: mp 171–172° (lit.[15] mp 171–172°); ir 3115, 1590, 1480, 1368, 1300, 1276, 1247, 1201, 1137, 1006, 960, 890, 770, 750 cm^{-1}. Product **14** was identical (mixture melting point, superimposable ir spectra) with an authentic sample of benzimidazole.

Reaction of 2-Phenylthio-3-phenylquinoxaline 1,4-Dioxide (8) or 2-Benzenesulfonyl-3-phenylquinoxaline 1,4-Dioxide (10) with Potassium Hydroxide.—In an erlenmeyer flask were placed 0.1 g of either **8** or **10** and 5 ml of 4% methanolic KOH solution. The solution was warmed for 2 hr, neutralized with HCl, and cooled in an ice bath. The crystals that formed were recrystallized from ethanol to give a product that was identical (mixture melting point, superimposable ir spectra) with 1-hydroxy-3-phenylquinoxalin-2-one 4-oxide (**9**).

Reaction of 1-Hydroxy-3-oxobenzimidazole-2-carboxamide ($4R_5$) with HCl.—In a round-bottomed flask equipped with a reflux condenser were placed 0.30 g of $4R_5$, 10 ml of H_2O, and 10 ml of concentrated HCl. The solution was refluxed for 12 hr, cooled, filtered, and neutralized with 40% KOH solution. The crystals that formed were collected, washed with water, and identified as a mixture of 1-hydroxy-3-oxobenzimidazole-2-carboxylic acid and its potassium salt $4R_{11}$.

Registry No.—$4R_1$, 15966-49-1; $4R_2$, 15966-52-6; $4R_3$, 31980-09-3; $4R_4$, 34759-66-5; $4R_5$, 34759-67-6; $4R_6$, 34759-68-7; $4R_7$, 34759-69-8; $4R_8$, 34759-70-1; $4R_9$, 34759-71-2; $4R_{10}$, 34759-72-3; $4R_{11}$, 34759-73-4; **8**, 34759-74-5; **9**, 33074-74-7; **10**, 34759-76-7.

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Sulfonium Salts. V. The Pummerer Reaction of Dibenzyl Sulfoxide

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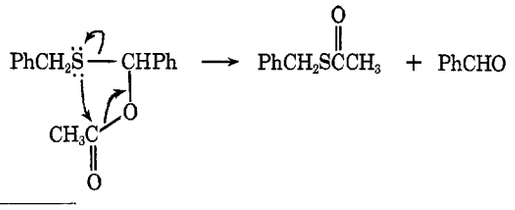
Dibenzyl sulfoxide reacts with acetic anhydride in chloroform and in carbon tetrachloride to provide α-acetoxybenzyl benzyl sulfide as the kinetically controlled product. Longer reaction times led to the products of thermodynamic control, α,α-bisbenzylthiotoluene and benzaldehyde. Benzyl sulfide and benzyl disulfide arise from attack of benzyl mercaptan on the intermediate acetoxysulfonium salt. A competitive kinetic isotope effect of *ca.* 9 characterizes the early stages of the Pummerer reaction.

Benzaldehyde, benzyl mercaptan, benzyl thiolacetate, and α,α-bisbenzylthiotoluene were reported in 1909 by Smythe[2] as the products[3] of the reaction of benzyl sulfoxide with acetic anhydride at 150°. Horner and Kaiser[4] reported that benzyl sulfoxide reacts slowly



with acetic anhydride in chloroform to provide benzaldehyde and benzyl thiolacetate, probably derived from α-acetoxybenzyl benzyl sulfide by an internal rearrangement, but no data supporting the structural assignments were given. The reaction with acetic anhydride has also been compared with the acid-catalyzed transformations of sulfoxides.[5]

Transformations of sulfoxides to α-acetoxy sulfides using acetic anhydride were observed by Pummerer[6] as early as 1909, and this classical reaction[6] bears his name. Since that time the scope of the reaction has been enlarged to encompass a group of similar reactions involving at some point reduction of a sulfonium sulfur atom in an organic molecule with subsequent oxidation of the α-carbon atom. Examples are varied, includ-

(1) Abstracted from a Ph.D. thesis to be submitted by C. J. Strong to the Graduate School of the Polytechnic Institute of Brooklyn in June 1973.

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(3) A recent review erroneously depicts the product as α-acetoxybenzyl benzyl sulfide: G. A. Russell and G. J. Mikol in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, p 157.

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