Sulfur Dioxide Extrusion from 1,3-Diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-Dioxides. A New Synthesis of 6-Phenylbenzo[*b*]phenazines[1,2]

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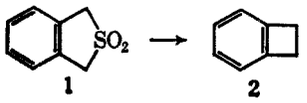
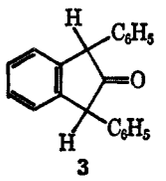
Pyrolysis of a *cis–trans* mixture of 1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**5**) produced 2,3-dibenzylquinoxaline (**12**), 6-phenylbenzo[*b*]phenazine (**13**), 3,4,7,8-tetraphenylbisquinoxalino[2,3-*a*:2′,3′-*e*]-cyclooctadiene (**14**), and 6-phenyl-5,12-dihydrobenzo[*b*]phenazine (**15**). Pyrolysis of *cis–trans* mixtures of 1-methyl- (**6**) and 1,3-dimethyl-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**7**) led, respectively, to 2-(α-methylbenzyl)- (**22**) and 2,3-bis(α-methylbenzyl)quinoxaline (**24**), in addition to 11-methyl-6-phenylbenzo[*b*]phenazine (**23**), obtained in both cases. Photolysis of a benzophenone-sensitized solution of **5** in dioxane produced only **12** as did sodium borohydride reduction of **5** in methanol. Alkaline hydrogen peroxide oxidation of **5** gave 2-benzyl-3-benzoylquinoxaline (**11**) while similar oxidation of **6** produced 2-(α-methylbenzyl)-3-benzoylquinoxaline (**31**). Chromic acid oxidation of **11** and **12** gave, ultimately, 2,3-dibenzoylquinoxaline (**27**); reduction of **27** under Wolff–Kishner conditions produced 1,4-diphenyl-2,3-diazaphenazine (**28**) as the major product. Sulfuric acid cyclodehydration of **11** and **31** led to **13** and **23**, respectively; similar treatment of 2-(α-bromomethyl)- (**32**) and 2-(α-hydroxybenzyl)-3-benzoylquinoxaline (**34**) gave, respectively, 11-bromo-6-phenylbenzo[*b*]phenazine (**33**) and **13**. Peracetic acid oxidation of **5** produced 2-benzyl-3-benzoylquinoxaline 1-oxide (**29**). Sodium hydrosulfite reduction of **29** led to **11**, while peracetic acid oxidation of **11** led to **29**. Similar peroxy acid oxidation of **6** gave only **31**. Sulfone **7** was unreactive to both alkaline and acid peroxide oxidation. Aromatic cyclodehydration of **29** with sulfuric acid led to 6-phenylbenzo[*b*]phenazine 12-oxide (**30**). Reduction of **30** with sodium hydrosulfite converted it into **15** which could then be oxidized to **13**; conversely, peroxy acid oxidation of **13** led only to **30**. Mechanisms for the pyrolytic, photolytic, and chemical extrusions of SO_2 from **5–7** are proposed. The condensation product between 1,3-diphenyl-2,4,5-trioxocyclopentane (**8**) and *o*-phenylenediamine was shown by nmr to exist entirely in the enol form, 1,3-diphenyl-2-hydroxy-Δ²-cyclopenta-[*b*]quinoxaline (**4b**). Methylation of **4b** gave only 1,4-dimethyl-1,3-diphenyl-4H-Δ³-cyclopenta[*b*]quinoxalin-2-one (**9**), while similar treatment of **5** led to **7** and 1,4-dimethyl-1,3-diphenyl-1,4-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**10**).

In 1959, Cava and Deana[4a] first reported that pyrolysis of 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**1**) led to the extrusion of sulfur dioxide with subsequent ring closure to benzocyclobutene (**2**). Since



1 **2**



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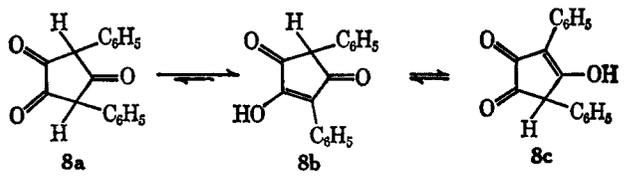
then, pyrolytic,[4b,c] photolytic,[4d,e] and chemical[5] eliminations of sulfur dioxide from certain benzylic sulfones have been utilized to prepare aromatic fused and/or substituted cyclobutenes.[6] The photochemical extrusion of carbon monoxide from α,α′-diphenyl cyclic ketones of type **3** provides an alternate facile entree into the cyclobutene system.[4e,7]

The reported preparation of 1,3-diphenylcyclopenta-[*b*]quinoxalin-2-one (**4a**)[8] and 1,3-diphenyl- (**5**)[9] and 1-methyl-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**6**)[10] provided obvious substrates for similar attempts to prepare cyclobuta[*b*]quinoxalines, three examples of which have been reported recently.[11]

This paper reports on the preparation and characterization of **4**, and the pyrolysis, photolysis, and chemical reactivity of **5**, **6**, and 1,3-dimethyl-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**7**).

1,3-Diphenyl-2-hydroxy-Δ²-cyclopenta[*b*]quinoxaline (4b).—The preparation reported for **4a** consisted of the condensation of the α diketone **8a**[12] with *o*-phenylenediamine.[8] The Claisen product **8a**, which was spectrally shown to exist entirely in the enol forms



8a **8b** **8c**

8b ⇌ **8c**, condensed with *o*-phenylenediamine to give a product (87%) whose melting point corresponded to

(1) This research was supported by the Department of the Army, U. S. Army Research and Development Command Office, Office of The Surgeon General, under Contract DA-49-193-MD-2992, and by Public Health Service Research Grant No. 1-RO1-A108-063-01 from the National Institute of Allergy and Infectious Diseases. This is Contribution No. 473 to the Army Research Program on Malaria.

(2) Presented before the Organic Division at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967; Abstracts of Papers, O-100.

(3) Taken entirely from the Ph.D. Theses of R. E. Misner and T. E. Brady, Fordham University, New York, N. Y., 1968.

(4) (a) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959); (b) M. P. Cava and R. L. Shirley, *ibid.*, **82**, 654 (1960); (c) M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960); (d) M. P. Cava, R. H. Schlessinger, and J. P. van Meter, *J. Amer. Chem. Soc.*, **86**, 3173 (1964); (e) M. P. Cava and D. Mangold, *Tetrahedron Lett.*, 1751 (1964).

(5) R. M. Dodson and A. G. Zielski, *Chem. Commun.*, 353 (1965).

(6) In the case of 2,4-diphenylthietane dioxides, pyrolysis has led to 1,2-diphenylcyclopropanes [R. M. Dodson and A. Klose, *Chem. Ind.* (London), 450, 1203 (1963)].

(7) G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlick, *Tetrahedron Lett.*, 1863 (1963).

(8) G. C. Chakravarti, *Quart. J. Indian Chem. Soc.*, **2**, 71 (1925).

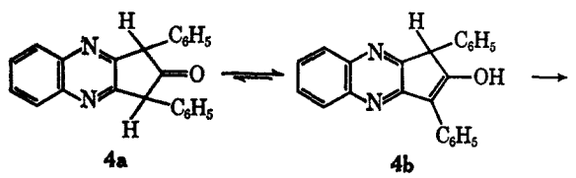
(9) C. G. Overberger, S. P. Lightheln, and E. A. Swire, *J. Amer. Chem. Soc.*, **72**, 2857 (1950).

(10) C. G. Overberger and J. M. Hoyt, *ibid.*, **73**, 3957 (1951).

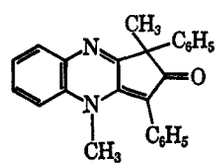
(11) (a) A. Fujuno, J. Kusuda, and T. Sakan, *Bull. Chem. Soc. Jap.*, **39** (1), 160 (1966); *Chem. Abstr.*, **64**, 12559*f* (1966); (b) W. Ried and W. Kunstmann, *Angew. Chem.*, **80**, 121 (1968); (c) S. Skujins and G. A. Webb, *Chem. Commun.*, 598 (1968). See also T. H. Markgraf and W. L. Scott, *ibid.*, 297 (1967), for a cyclobuta[*b*]quinoline.

(12) L. Claisen and T. Ewan, *Ann.*, **284**, 250 (1895).

that reported by Chakravarti.[8] This condensation product showed no carbonyl absorption in the ir, and its nmr spectrum displayed three peaks at δ 12.21 (broad singlet, 1, OH), 8.00–7.25 (m, 14, aromatic), and 4.40 (s, 1, CH). Clearly, this quinoxaline derivative existed entirely as the enol **4b**. Pyrolysis and photolysis of **4b** led only to recovery of starting material. Treatment of **4b** with potassium *t*-butoxide and methyl iodide led only to the isolation of 1,4-dimethyl-



4a **4b**



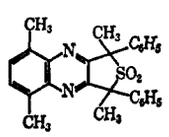
9

1,3-diphenyl-4H-Δ^3-cyclopenta[*b*]quinoxalin-2-one (**9**), in 30% yield.

Preparation and Pyrolysis of 5, 6, and 7 (Scheme I).—Sulfones **5** (as a *cis–trans* mixture,[13] 93%) and **6** (87%) were prepared by the procedures of Overberger and coworkers,[9,10] *via* the condensation of *o*-phenylenediamine and the appropriate α diketone, 2,5-diphenyl- and 2-methyl-2,5-diphenyl-3-keto-4-hydroxy-2,3-dihydrothiophene 1,1-dioxide, respectively. Treatment of **5** with potassium *t*-butoxide and excess methyl iodide led to **7** (as an inseparable 35:65 *cis–trans* mixture,[14] 16%), in addition to 1,4-dimethyl-1,3-diphenyl-1,4-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**10**, 40%)[15,16] and 2-benzyl-3-benzoylquinoxaline (**11**, 3%).[16]

(13) Based on analogy to **7** whose nmr[14] clearly establishes its *cis–trans* nature. Sulfone **5** was too insoluble for such analysis.

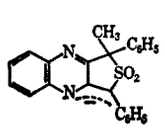
(14) Nmr ($CDCl_3$): δ 8.05 (m, 4, aromatic), 7.20 (*trans*) and 7.07 (*cis*) (each s, total 10, C_6H_5, area ratio 35:65 *cis–trans*), and 2.24 (*cis*) and 2.12 (*trans*) (each s, total 6, CH_3, area ratio 35:65 *cis–trans*). In the *trans* isomer, the protons of each methyl group are in the shielding region of a phenyl substituent, while, in the *cis* isomer, each phenyl group shields the other. In only one case, 1,3,5,8-tetramethyl-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (i) have we been able to partially separate the *trans* isomer from the mixture.



i

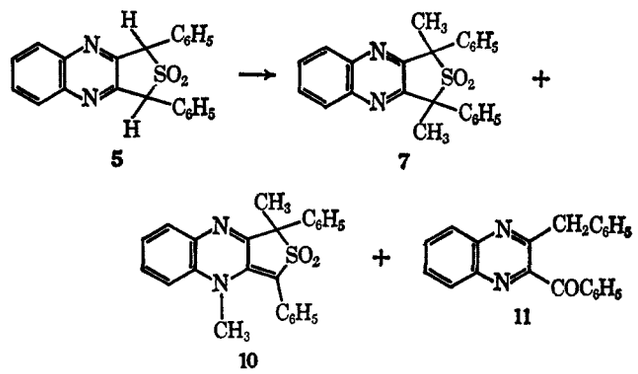
(15) In both **9** and **10**, the NCH_3 protons appeared as a singlet downfield relative to the CCH_3 by 1.42 and 0.84 ppm, respectively.

(16) The formation of both **7** and **10** can be accounted for by the further methylation of the delocalized anion ii formed initially from **6**.



ii

In the presence of 1 equiv of KO-*t*-Bu and CH_3I and using a short reaction time, **6** was isolated. Further methylation of **6** converted it into the mixture of **7** and 10. Quinoxaline **11** was not obtained when the reaction was run under nitrogen. It must therefore be a product of the air oxidation of **5**.



5 **7**

10 **11**

Pyrolysis of **5** under a variety of conditions (Table I) produced the known 2,3-dibenzylquinoxaline (**12**),[17] 6-phenylbenzo[*b*]phenazine (**13**), 3,4,7,8-tetraphenylbisquinoxalino[2,3-*a*:2′,3′-*e*]cyclooctadiene (**14**), and, in one instance, 6-phenyl-5,12-dihydrobenzo[*b*]phenazine (**15**).[18]

TABLE I

PYROLYSIS OF 5

Matrix	Reaction temp, °C	Products, % yield 12	13	14	15
Ethylene glycol	180	14	32		
Diethylene glycol	240	8	32		
Dimethyl phthalate	260		30	6	
Triethylene glycol	280	5	6		27
$NaHCO_3$[a]	550		22	27	

[a] Solid–solid reaction.

The 6-phenylbenzo[*b*]phenazine (**13**) [$\lambda_{max}^{95\%EtOH}$ 210 mμ (ϵ 20,000), 252 (27,000), and 285 (83,000)] was obtained as a brilliant red crystalline material whose most striking spectral feature was the display of a deshielded proton on C-11 appearing as a singlet at δ 8.95.[19] Further, the small but perceptible conjugative effect in the uv relative to **16**[19] suggests a considerably nonplanar conformation of the C-6 phenyl substituent. Ultimately, **13** was independently prepared by the sulfuric acid catalyzed aromatic cyclodehydration of 2-benzyl-3-benzoylquinoxaline (**11**) (*vide infra*).

The formation of dimers under pyrolytic conditions is precedented,[4a,20a] and the structure of **14** was based, *inter alia*, on a molecular weight, and an nmr spectrum which showed a 4 H singlet at δ 5.56 and a complex aromatic multiplet (8.20–7.20) in the ratio of 1:7, respectively.[20b] In the uv, the bathochromic shift (50 mμ) of dimer **14** compared with that of **12** suggests a tub form (**14a**) which would allow considerable overlap of the π electrons of the aromatic nuclei.[20a] All

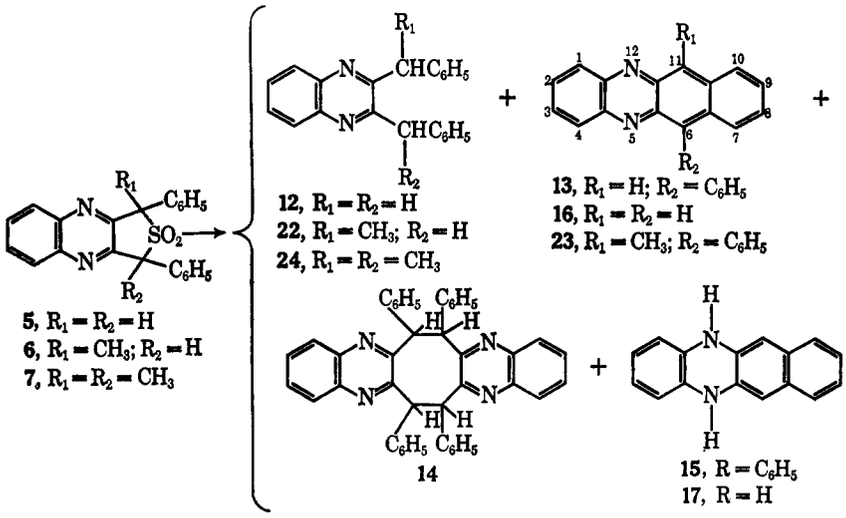
(17) P. Ruggli and P. Zeller, *Helv. Chim. Acta*, **28**, 741 (1945).

(18) Under all conditions reported in Table I, polymeric and tarry products (40–50%) were obtained. In the solid reaction with sodium bicarbonate, thin layer chromatography (tlc) indicated the presence of at least 17 different products, only two of which (**13** and **14**) could be identified.

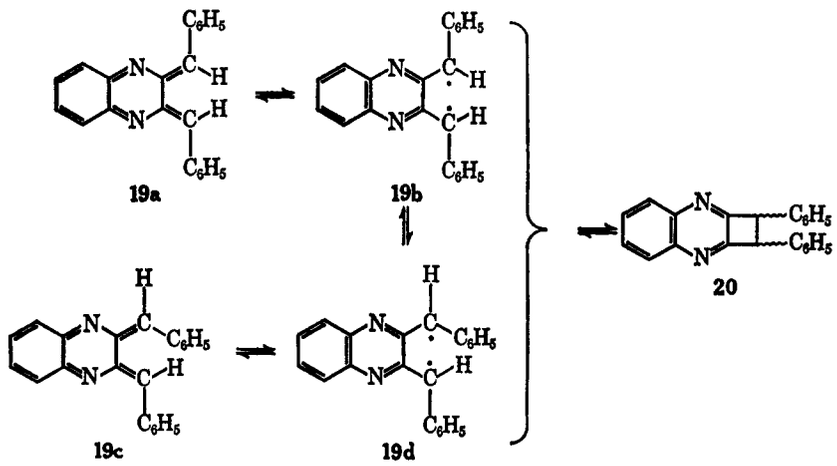
(19) Benzo[*b*]phenazine (**16**) prepared by the procedure of G. Hinsberg [*Ann.*, **319**, 257 (1901)] showed a $\lambda_{max}^{95\%EtOH}$ 210 mμ (ϵ 13,000), 250 (25,000), and 281 (80,000); $\delta_{TMS}^{DMSO\text{-}d_6}$ 8.89 (s, 2, C-6, 11 hydrogens) as well as 8.40–7.72 (m, 8, aromatic).

(20) (a) J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2708 (1963). (b) Dimer **14** contains four asymmetric C atoms. The product obtained must be a mixture of isomers.

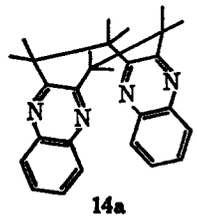
SCHEME I



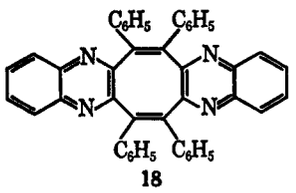
SCHEME II



attempts to oxidize **14** to the extremely crowded cyclooctatetraene derivative **18** were unsuccessful.



14a



18

The light green pyrolysis product **15** was identical with that obtained *via* the catalytic reduction of **13** over Pd–C.[21] Dihydro derivative **15** is unstable in both solid state and solution and is rapidly air oxidized to **13**.

The Woodward–Hoffmann rules predict that pyrolysis of a *cis–trans* **5** mixture would lead to a concerted disrotatory process[22a,b] to the isomeric *o*-quinodimethanes **19a** and **19c**,[4a–c,22c] or to the diradicals **19b** and **19d** (depending on the multiplicity of the excited state), either or both of which are in equilibrium with the thermally labile quinoxaline[2,3-*c*]cyclobutene (**20**) (Scheme II). Although these primary pyrolysis intermediates could not be trapped,[23] **12**, **13**, and **14** can be explained as rational transformation products of the very reactive **19**. Thus hydrogen abstraction from solvent (or **5**) would yield **12**, dimerization would lead to **14**, and a precedented[4c,24,25–27] intramolecular cyclization[28] of **19c** would produce **13** *via* the allyl isomers **21a** ⇌ **21b**.[29] The suggestion that **12** and **14** arise from the common intermediate **19** is consistent with the formation of **12** only in protic media and **14** only in

(21) Its nmr spectrum also displayed the C-11 proton singlet at δ 8.68. The uv spectrum of freshly prepared, blue-fluorescent **15** [$\lambda_{max}^{95\%EtOH}$ 247 mμ (ϵ 14,000), 280 sh (18,000), and 288 (28,000)] compared favorably with that of the blue-fluorescent 5,12-dihydrobenzo[*b*] phenazine (**17**) [$\lambda_{max}^{95\%EtOH}$ 248 mμ (ϵ 17,000), 283 (33,000), and 286 sh (31,000)] prepared *via* Hinsberg's procedure.[19] Unlike **15**, however, the dihydro derivative **17** is very stable and its reoxidation to **16** can only be effected with sodium dichromate in acetic acid.[19]

(22) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. G. McGregor and D. A. Lemal, *ibid.*, **88**, 2858 (1966); (c) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).

(23) By thermolysis of **5** in the presence of dienophilic scavengers, 1,4-naphthoquinone and 1,3-diphenylisobenzofuran.

(24) F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.*, **80**, 6149 (1958).

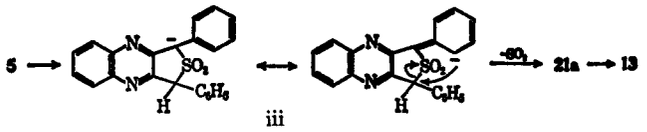
(25) H. Kloosterziel and H. J. Backer, *Rec. Trav. Chim.*, **71**, 1235 (1951).

(26) G. Wittig and M. Leo, *Chem. Ber.*, **64B**, 2395 (1931).

(27) H. Staudinger and F. Pfenninger, *ibid.*, **49**, 1941 (1916).

(28) This concerted process would relieve the severe steric interaction between the phenyl and vinyl hydrogens as suggested by models.

(29) A possible alternate route to **13** is the formation of carbanion iii (thermally or in the presence of even a weak base) from **5** followed by intra-



iii

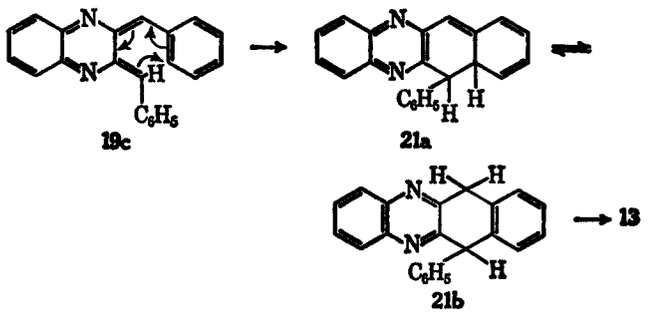
molecular nucleophilic displacement of the SO_2 [*cf.* H. Drews and E. K. Fields, *Chem. Ind.* (London), 143 (1961)].

TABLE II

MASS SPECTRUM OF 5[a]

m/e	Peak height, arbitrary scale divisions	Relative intensity	Our spectrum of SO_2
47	0		
48	131	70.0	69.0
49	3		
50	18		
51	37		
63	15		
64	187	100.0	100.0
65	6		
66	10		
101	9		
101 − ⅓	5		
101 − ⅔	7		
102	15	3.1	Triply charged ions
102 − ⅓	3		
102 − ⅔	3		
103	5		
152 − ½	138		
153	141	29.2	Doubly charged ions
153 − ½	56		
154	60		
154 − ½	14		
305	427	88.4	
306	483	100.0	
307	190	39.3	
308	442	91.5	
309	124	25.7	
310	29	6.0	
311	6	1.2	
338	7	1.4	
	Low-voltage measurements[b]		
305	37	2.2	
306	1648	100.0	
307	443	26.9	
308	1484	90.0	
309	378	22.9	
310	97	5.9	
311	17	1.0	
338	26	1.6	

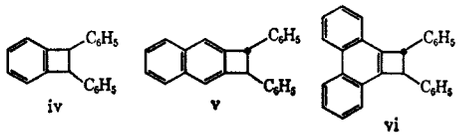
[a] See ref 32. [b] Ionizing voltage = 7.5 V, uncorrected.



dimethyl phthalate and the solid-state fusion with sodium bicarbonate (Table I). Like its benzene[4c] and naphthalene[4d] analogs, the effective pyrolysis temperature of sulfone **5** must be higher than the temperature at which the thermally labile **20** must rearrange to secondary pyrolysis products.[30] Finally, since **15** was not obtained at the lower pyrolysis temperature, its formation seems to be an oxidation–reduction[31] reaction involving **15**, unreacted **5** and/or SO_2, and/or the glycol matrix.

The mass spectrum of **5**[32] (Table II), showed no trace at *m/e* 372 corresponding to its molecular weight. By far the strongest peaks in the spectrum occur in the mass region 305 to 310. At low voltage, intensities at *m/e* 305 and 307 drop, but intensity distribution over *m/e* 306, 308, 310, and 338 remain essentially constant, and the peaks at *m/e* 306 and 308 stand out prominently over all others. Moreover, the second most intense group of peaks in the 70-V spectrum corresponds to doubly charged ions of masses 305 to 309, and the spectrum shows a group of peaks, though considerably less intense, corresponding to triply charged ions of masses 304 to 308. Evidently, the major components contributing to the spectrum are highly stable, radiation-resistant species of masses 306 and 308. The *m/e* 308 peak can be ascribed to **20**, or **21a** ⇌ **21b**, while the peak at *m/e* 306 must be due to **13**. The small peak at *m/e* 310 can be assigned to **12**. Thus **5**

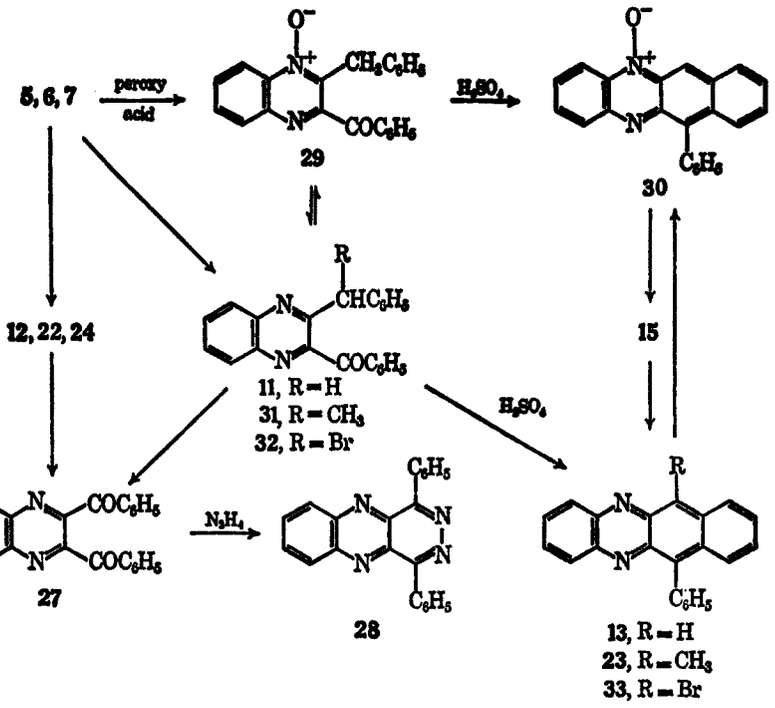
(30) Thus, iv,[4c,24] v,[4d] and vi,[4e] independently prepared, thermally rearrange to their respective dihydroanthracene, -naphthacene, and -dibenz[*a*,*c*]anthracene derivatives.



(31) Only in this pyrolysis was hydrogen sulfide evolved.

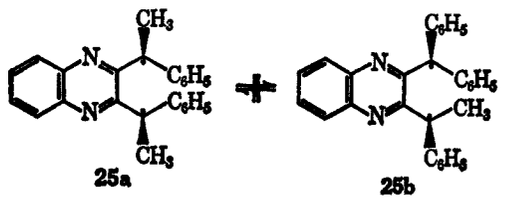
(32) We are grateful to Mr. Seymour Meyerson and Dr. Ellis K. Fields for determining the mass spectrum of **5** and its interpretation.

SCHEME III



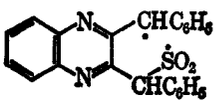
must have decomposed thermally in the inlet system (temperature 325°, pressure 20–50 μ Hg). The view that the mass spectrum is due to thermolysis products gains additional support from prominent peaks at masses **48** and **64**, standing out prominently above neighboring peaks and almost certainly due to SO_2.[32,33]

Pyrolysis of **6** and **7** at 180° for 3–4 hr led only to recovery of starting material. At 240°, however, **6** gave 2-(α-methylbenzyl)-3-benzylquinoxaline (**22**, 12%) and 11-methyl-6-phenylbenzo[*b*]phenazine (**23**, 22%) with a 38% recovery of unreacted **6**. At 280°, **7** (35:65 *cis–trans* mixture) led to **23** (4%) and an inseparable 38:62 *meso–dl* mixture of 2,3-bis(α-methylbenzyl)quinoxaline (**24**, 14%), with a 32% recovery of unreacted **7**. The conversion **7** → **24** seems to be very nearly stereospecific; *i.e.*, the ratio of diastereoisomers in the product mixture **24** is very nearly equal to the ratio of geometric isomers in reactant mixture **7**. This suggests that intermediates **25a** and **25b** once formed do not interconvert, and that hydrogen addition to these diradicals must occur in the same manner. Thus, *cis* **7** would lead to *meso* **24** *via* planar **25a** while *trans* **7** would proceed to *dl* **24** *via* **25b**.



25a **25b**

Photolysis of 5.—A benzophenone-sensitized solution of **5** in dioxane was irradiated, under nitrogen, with a 125-W Hanovia medium pressure Hg arc for 48 hr. Evaporation of the solvent followed by chromatography of the residue over alumina led only to **12** (23%) and considerable amounts of tars. Assuming the photolytic process to occur *via* homolytic cleavage of the C–S bond,[4d,34] the initially formed **26** would then lose SO_2 to form a **19b–19d** mixture. Hydrogen abstractions from solvent by these biradicals to form **12** must proceed at a



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rate greater than all other processes of dimerization and intramolecular cyclization. The insolubility of **5** in most organic solvents precluded any significant solvent study.[13]

Chemical Reactivity of 5, 6, and 7 (Scheme III).—Treatment of a suspension of **5** in ethanol with equimolar amounts of hydrogen peroxide and sodium hydroxide resulted in a vigorous reaction from which **11** was isolated in 85% yield. The monomethyl derivative **6** underwent a similar reaction to give 2-(α-methylbenzyl)-3-benzoylquinoxaline (**31**, 69%) while **7** did not react. The unprecedented reduction of **5** with sodium borohydride in methanol gave **12** (74%)[35] while **6** led to **22** (29%). Oxidation of **12** and **11** with excess chromic acid converted each into 2,3-dibenzoylquinoxaline (**27**) (80 and 93%, respectively), while a limited amount of oxidant converted **12** into **11** and **27**. Selenium dioxide in dioxane also oxidized **11** to **27** (52%). Reduction of **27** in ethylene glycol with 85% hydrazine hydrate and sodium hydroxide led to both the Wolff–Kishner product **12** (2%) and 1,4-diphenyl-2,3-diazaphenazine (**28**, 43%).[36] The latter condensation

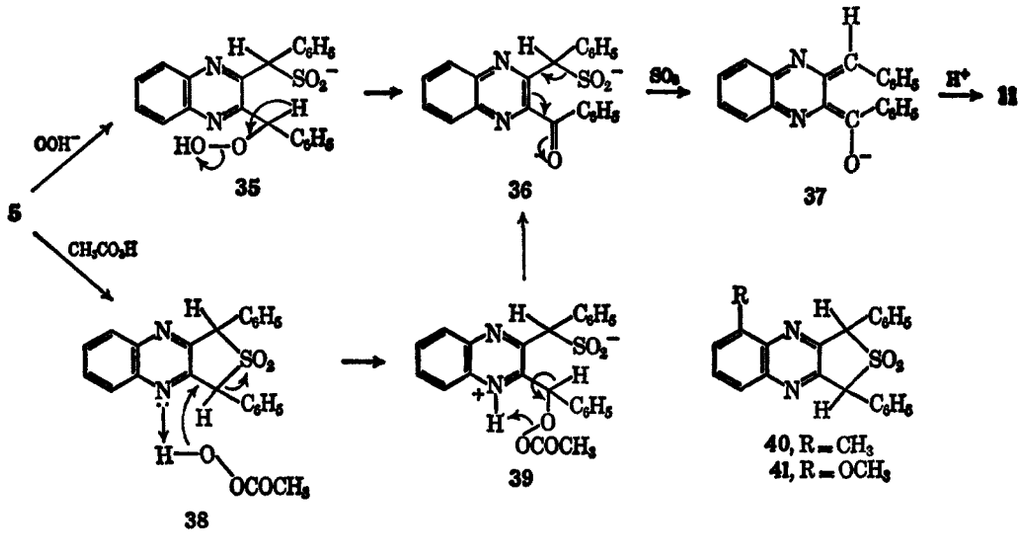
(33) Generally, if SO_2 is lost in an ionic process under electron impact, it does not take the charge and therefore it is not observed directly in the spectrum.

(34) P. B. Asycough, K. J. Ivin, and J. H. O'Donnell, *Trans. Faraday Soc.*, **61**, 1110 (1965).

(35) Equilibration studies using CH_3OD and $NaOCH_3$ (followed by D_2O hydrolysis) and reductions with $NaBH_4$ in CH_3OD and $NaBD_4$ in CH_3OH suggest initial hydride attack on **5**, followed by SO_2 extrusion, and proton abstraction to give **12**. Reduction of **5** with ω-Raney nickel led to **12** in 48% yield.

(36) This seems to be the first authentic example of the 2,3-diazaphenazine system: *cf.* J. Wegler, *J. Prakt. Chem.*, **143**, 135 (1935). In the absence of sodium hydroxide, the yield of **28** rose to 73%, while none of **12** was isolated. After this work was completed, M. J. Haddadin and C. H. Issidorides [*Tetrahedron Lett.*, 4609 (1968)] communicated the isolation of 1-phenyl-2,3-diazaphenazine.

SCHEME IV



product is thermally stable and resistant to further oxidation and reduction.

Aromatic cyclodehydration[37,38] of **11** with concentrated sulfuric acid led to **13** (85%) after heating for 5 min on a steam bath. This synthetic route to 6-phenylbenzo[*b*]phenazines using concentrated sulfuric acid or polyphosphoric acid seems to be a general one.[39] Thus, **31**, 2-(α-bromomethyl)-3-benzoylquinoxaline (**32**),[40] and 2-(α-hydroxybenzyl)-2-benzylquinoxaline (**34**)[41] led, respectively, to **23** (78%), 11-bromo-6-phenylbenzo[*b*]phenazine (**33**, 84%), and **13** (62%).

Treatment of **5** in chloroform with 2 equiv of peroxy acid (*m*-chloroperbenzoic acid, peracetic acid, or hydrogen peroxide in acetic acid) also resulted in the extrusion of SO_2 to give ultimately 2-benzyl-3-benzoylquinoxaline 1-oxide (**29**, 32–47%). With 1 equiv of peroxy acid, **29** (30%) was also obtained, together with 45% unreacted **5**. When the oxidation was quenched before reaction was complete, both **11** and **29** were isolated, suggesting that **11** was the precursor of **29** after the oxidative extrusion of SO_2. Both were interrelated by oxidation of **11** with peracetic acid to **29** (76%), while the reduction of **29** with sodium hydrosulfite[42] led to **11**. Although peracetic acid oxidation converted **6** into **31** (60%), the reaction must be sensitive to steric influences, since **7** was recovered unchanged under identical oxidative conditions.

The site of the N-oxide function in **29** was based on its cyclodehydration with concentrated sulfuric acid to 6-phenylbenzo[*b*]phenazine 12-oxide (**30**) in 66% yield. The C-1 and C-11 hydrogens, *peri* to the N-oxide function, now show the expected deshielding[43] (δ 8.66 m and 9.35 s, respectively), the latter appearing even further downfield than the C-11 hydrogen in **13**. Reduction of **30** with sodium hydrosulfite converted it into **15** (75%) which could then be oxidized to **13**; conversely, peroxy acid oxidation of **13** led only to **30** (67%).

Reaction Mechanism (Scheme IV).—Alkaline hydrogen peroxide extrusion of SO_2 from **5** and **6** can be depicted simply as occurring with initial nucleophilic attack on the α carbon by the perhydroxyl anion to give the hydroperoxide **35**.[44] Attack of base on the α hydrogen of this allyl hydroperoxide **35** results in the formation of ketone **36**,[45] enolization of which facilitates the loss of SO_2 to form **37**.[46] Regeneration of the ketonic moiety accompanied by proton addition would lead finally to **11**. The intermediacy of the perhydroxyl anion dictates an indiscriminate attack on both α carbons in sulfone **5**, and this has been observed with both 5-methyl- (**40**) and 5-methoxy-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (**41**) to give two ketones in each case.[47]

In the presence of peracetic acid, oxidative extrusion from **5** to **6** is believed to commence with coordination of the peroxy acid molecule with the nitrogen (as in **38**). Transfer of the NH proton to the acetate anion leaving group (**39**) would then proceed *via* **36** → **37**, to **11**, further peroxidation of which would lead to the observed product **29**. Since attack on **6** by OOH^- and peroxy acid occurs only at the less hindered side to give **31**, the sterically hindered α carbons in **7** consequently are unresponsive to both the nucleophilic and electrophilic oxidants. In the case of oxidation product **31** (from **6**), the combined steric effect on one side and electron-withdrawing influence of the $-COC_6H_5$ substituent on the other prevent further peroxidation at either nitrogen.[48]

Finally, bromination of **12** in carbon tetrachloride with 2 equiv of NBS gave a 63% mixture of *meso*- and *dl*-2,3-bis(α-bromobenzyl)quinoxaline (**42**). A Finkelstein reaction (sodium iodide in acetone) on **42** was un-

(37) C. K. Bradsher, *Chem. Rev.*, **38**, 447 (1946).

(38) F. A. Vingiello and J. R. Thornton, *J. Org. Chem.*, **31**, 659 (1966).

(39) The remarkably few benzo[*b*]phenazines available (G. A. Swan and D. G. I. Felton in "The Chemistry of Heterocyclic Compounds," Vol. II, A. Weissberger Ed., Interscience, New York, N. Y. 1957, pp 213–216) have all been prepared by condensation of the appropriate naphthalene derivative with *o*-phenylenediamine.

(40) Prepared in 48% yield by bromination of **11** in CCl_4 with NBS under irradiation with a high intensity lamp.

(41) Prepared in 75% yield by sodium borohydride reduction of **11** in the presence of sodium hydroxide.

(42) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Amer. Chem. Soc.*, **80**, 3009 (1958).

(43) Y. Morita, *Chem. Pharm. Bull. Tokyo*, **14**, 419 (1966).

(44) J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience, New York, N. Y., 1962, pp 11–28.

(45) H. G. Davies, "Organic Peroxides," Butterworth, London, 1961, Chapter 13.

(46) This is somewhat analogous to the decarboxylation of β-keto acids.

(47) E. J. Moriconi, T. E. Brady, and R. E. Misner, unpublished work.

successful in converting it into a cyclobutene derivative, as was treatment of **34** with dicyclohexylcarbodiimide.

Experimental Section[49]

1,3-Diphenyl-2-hydroxy-Δ^2-cyclopenta[*b*]quinoxaline (4b) was prepared in 89% yield by Chakravarti's procedure:[8] mp 253–254° (lit.[8] mp 253°); ir (KBr) 6.10 μ (enol C=C); uv max (95% EtOH) 224 mμ (ϵ 22,000), 266 (13,400), 310 (11,600), and 325 (10,000); nmr (DMSO-d_6) δ 12.21 (broad singlet, 1, OH), *ca.* 8.00–7.25 (m, 14, aromatic), and 4.40 (s, 1, CH).

Preparation of 1,4-Dimethyl-1,3-diphenyl-4H-Δ^3-cyclopenta[*b*]quinoxaline-2-one (9).—Potassium *t*-butoxide (0.80 g, 7.1 mmol) was added to a suspension of **4b** (1 g, 2.98 mmol) in 50 ml of dry *t*-BuOH and the whole was refluxed for 1 hr and then cooled to ambient temperature. A solution of 3 ml (5.1 g, 0.036 mol) of CH_3I in 10 ml of *t*-BuOH was added and the solution was refluxed for an additional 2 hr. The green solution was cooled, added to 200 ml of ice, and then extracted with two 100-ml portions of ether. The combined ether extracts were dried (Na_2SO_4) and evaporated to a yellow-green oil. The oil was dissolved in 5 ml of CH_2Cl_2 and deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I). The column was eluted with 1 l. of ether. The ether was evaporated *in vacuo* to yield 0.32 g (30%) of **9** as yellow-green needles: mp 177–178° (from CH_3OH); ir (KBr) 6.00 μ (C=O); uv max (95% EtOH) 222 mμ (ϵ 21,500), 226 (22,000), 263 (10,200), 306 (10,000), and 323 (8700); nmr ($CDCl_3$) δ 7.85–7.20 (m, 14, aromatic), 3.25 (s, 3, NCH_3), and 1.83 (s, 3, CCH_3).

Anal. Calcd for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53; N, 7.69; mol wt, 364. Found: C, 82.26; H, 5.37; N, 7.92; mol wt. 355 (isothermal distillation).

1,3-Diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (5) was prepared in 93% yield by the procedure of Overberger, Lightheln, and Swire:[9] darkened at 220° with decomposition between 243 and 254°; ir (KBr) 7.50, 8.56, and 8.95 μ (SO_2); uv (95% EtOH) 222 mμ (ϵ 37,000), 240 (36,000), 297 (10,800), and 327 (8300).

Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.94; H, 4.33. Found: C, 70.97; H, 4.35.

1,3-Diphenyl-1-methyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (6) was prepared in 87% yield by the procedure of Overberger and Hoyt:[10] mp 206–207° (lit.[10] mp 206–207°); ir (KBr) 7.52, 8.80, and 8.85 μ (SO_2); uv max (95% EtOH) 241 mμ (ϵ 34,000) and 324 (7200); nmr ($CDCl_3$) δ 8.17 (A_2B_2 multiplet, 4, quinoxaline), 7.52 (s, 10, C_6H_5), 5.72 (s, 1, CH), and 2.38 (s, 3, CH_3).

Reaction of 5 with KO-*t*-Bu and CH_3I.—KO-*t*-Bu (1.5 g, 13.4 mmol) was added in one portion to 2.0 g (5.4 mmol) of **5** suspended in 50 ml of dry *t*-BuOH (distilled over potassium). The suspension was refluxed until a dark red homogeneous solution was obtained. The solution was cooled to room temperature and an excess of CH_3I (5 ml, 8.5 g, 0.06 mol) in 10 ml of dry *t*-BuOH was added dropwise (10 min) to the stirred solution. The solution was then refluxed for an additional 2 hr. On heating, the dark red colored solution initially darkened and then lightened to a yellow solution, at which time a highly fluorescent yellow solid became visible. The mixture was cooled and added to 200 ml of an ice–water mixture and the whole treated with two 100-ml portions of ether. Each time, the bright yellow insoluble solid which formed between the two layers was filtered to yield a total of 0.92 g (40%) of crude **1,4-dimethyl-1,3-diphenyl-1,4-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxide (10)** as brilliant yellow plates: mp 236–236.5° (from CH_3OH; Norit); ir (KBr) 7.82, 7.90, and 8.82 μ (SO_2); uv max (95% EtOH) 219 mμ (ϵ 37,000), 245 (53,000), and 327 (13,000); nmr ($CDCl_3$) δ 7.70–6.90 (m, 14, aromatic), 3.06 (s, 3, NCH_3), and 2.22 (s, 3, CCH_3).

Anal. Calcd for $C_{24}H_{20}N_2O_2S$: C, 71.97; H, 5.03; N, 6.99; mol wt, 400. Found: C, 72.19; H, 5.00; N, 7.20; mol wt, 410 (Rast).

The two layer filtrates were separated and the combined ether layers were washed successively with 100 ml of H_2O, 100 ml of 10% HCl, and 100 ml of H_2O. The ether solution was dried (Na_2SO_4), and evaporated to a dark orange oil which was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I). Elution with hexane produced a small amount of a tan solid, identified as **2-benzyl-3-benzoylquinoxaline (11,** 0.05 g, 3%), mp 96–97° (*vide infra*). Continued elution with 1:1 hexane–ether resulted in the isolation of 0.35 g (16%) of an inseparable mixture of *cis*- and *trans*-**1,3-dimethyl-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline 2,2-dioxides (7):** mp 200–204°; ir (KBr) 7.63, 8.70 and 8.75 μ (SO_2); uv (95% EtOH) 241 mμ (ϵ 30,500) and 325 (7600).

Anal. Calcd for $C_{24}H_{20}N_2O_2S$: C, 71.98; H, 5.03; N, 6.99; mol wt, 400. Found: C, 72.06; H, 5.11; N, 7.14; mol wt, 384 (isothermal distillation).

Pyrolysis of 5–$NaHCO_3$ Mixture.—A mixture (mortar and pestle) of **5** (1 g, 2.7 mmol) and 5.0 g of anhydrous $NaHCO_3$ was heated in an open evaporating dish over a Bunsen flame until it turned deep red (*ca.* 5 min, slight charring). The solid pyrolysate was then extracted with 200 ml of CH_2Cl_2 (Soxhlet) until further washings were colorless. The extract was evaporated *in vacuo* and the residue was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I). The column was eluted successively with 1:1 CCl_4–CH_2Cl_2, and CH_2Cl_2, each elution being continued until the eluent became colorless.

1:1 CCl_4–CH_2Cl_2 Fraction.—Evaporation of the eluate *in vacuo* led to a dark red tarry residue, shown by tlc to contain one major and five minor components. Chromatography of the residue on a 2.5 × 25 cm column of Florisil (60–200 mesh) with 1:4 CH_2Cl_2–CCl_4 led to ten 100-ml fractions. Fractions 4–8 were combined, reduced in volume to 10 ml (steam bath), and rechromatographed on Florisil (eluent, CCl_4) to give ultimately 0.206 g (27%) of **1,2,5,6-bis(2,3-quinoxalino)-3,4,7,8-tetraphenylcyclooctadiene (14):** softened at 190°, mp 203–205°; uv max (95% EtOH) 254 mμ (ϵ 14,000) and 288 (48,500); nmr ($CDCl_3$) δ 8.40–7.00 (m, 28, aromatic) and 5.56 (s, 4, CH).

Anal. Calcd for $C_{44}H_{32}N_4$: C, 85.68; H, 5.23; N, 9.08; mol wt, 612. Found: C, 85.42; H, 5.45; N, 9.13; mol wt, 582 (isothermal distillation).

CH_2Cl_2 Fraction.—Evaporation of the eluate *in vacuo* led to 0.19 g (22%) of crude **6-phenylbenzo[*b*]phenazine (13).** One recrystallization from 1,2-dichloroethane gave pure **13** as tiny red needles: mp 254–255°; nmr[50] ($CDCl_3$) δ 8.95 (s, 1, C-11 hydrogen), 8.30–7.40 (m, 8, aromatic), and 7.60 (s, 5, C_6H_5).

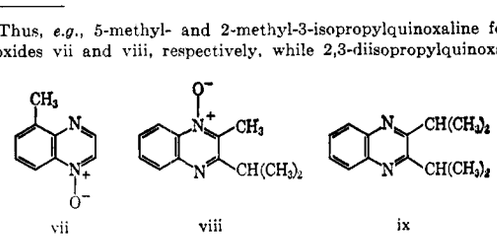
Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.15; mol wt, 306. Found: C, 86.29; H, 4.56; N, 9.15; mol wt, 306 (*m/e*), 300 (Rast).

Pyrolysis of 5 in Solution.—One gram (2.7 mmol) of **5** suspended in 30 ml of ethylene glycol was refluxed for 2 hr at 200° (Wood's metal bath). On heating, the solid dissolved slowly and the entire solution turned a deep red. The glycol solution was cooled and added to 50 ml of water. The resultant brown solid was filtered, dried, and deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I) with 5 ml of CH_2Cl_2. Elution of the column with 1:1 pentane–ether produced two colored fractions, one pink (250 ml) and the second orange (200 ml). On evaporation of the eluate (Rinco), the pink fraction yielded 0.11 g (14%) of **2,3-dibenzylquinoxaline (12)** as long white needles: mp 118–118.5° (from hexane, Norit) (lit.[17] mp 117–118°); uv max (95% EtOH) 239 mμ (ϵ 37,000), 294 sh (9500), and 320 (17,000); nmr (CCl_4) δ 8.20–7.50 (m, 4, quinoxaline), 7.20 (s, 10, C_6H_5), and 4.29 (s, 4, CH_2).

Evaporation of the orange fraction (Rinco) gave 0.27 g (32%) of **13.**

The pyrolysis of **5** (2 g, 5.4 mmol) suspended in 25 ml of tri-

(48) Thus, *e.g.*, 5-methyl- and 2-methyl-3-isopropylquinoxaline form only the N-oxides vii and viii, respectively, while 2,3-diisopropylquinoxaline (ix)



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is recovered unchanged from peroxy acid [J. K. Landquist, *J. Chem. Soc.*, 2816 (1953); J. K. Landquist and G. J. Stacey, *ibid.*, 2822 (1953)]. In addition, **27** did not form an N-oxide with peroxy acids.

(49) (a) Melting points were determined on a Koffler hot-stage melting point apparatus and are corrected; (b) the ir spectra were recorded on a Model 337 Perkin-Elmer grating spectrophotometer; (c) the uv spectra were recorded on a Cary 15 dual-beam recording spectrophotometer; (d) unless otherwise stated, the nmr spectra were obtained on a Varian Associates Model A-60 spectrometer using dilute (*ca.* 100 mg/ml) solutions, and chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane.

(50) We are grateful to Leroy F. Johnson, Varian Associates, for obtaining the 100-Mc nmr spectrum of this compound.

ethylene glycol led to a dark green mixture which was added to 100 ml of an ice–water mixture. The resulting emulsion was extracted with 500 ml of pentane. Evaporation of the pentane extracts (Rinco) left **6-phenyl-5,12-dihydrobenzo[*b*]phenazine (15)** (0.38 g, 27%) as a yellow solid: darkened at 160°, mp 205–207° dec; ir (KBr) 2.99 and 3.04 μ (NH); nmr (DMSO-d_6) δ 8.28 (s, 1, C-11 hydrogen), 7.80–7.00 (m, 8, aromatic), 6.94 (s, 5, C_6H_5), and 6.25 (broad mound, 2, NH). This material was unstable in the solid state and in solution and was rapidly oxidized to **13**.

The aqueous glycol solution was then extracted with 200 ml of CH_2Cl_2. The methylene chloride extracts were evaporated to dryness (Rinco); the residue was deposited on an 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I) and eluted with 500 ml of 1:1 ether–pentane solution. The first 150 ml led, after evaporation, to 0.1 g (5%) of **12**, while evaporation of the remaining eluate ultimately gave 0.12 g (6%) of **13**. A final elution of the column with ether led only to tars.

Compound **15** was also prepared by the catalytic reduction of **13** and by the sodium hydrosulfite reduction of 6-phenylbenzo[*b*]-phenazine 12-oxide (**30**):

Catalytic Reduction of 13.—A suspension of 1 g (3.2 mmol) of **13** and 5% Pd–C in 125 ml of ethyl acetate was hydrogenated at 50 psi (Paar shaker) for 3 hr. The catalyst was removed, and the solvent was evaporated (Rinco) to yield **15** (0.56 g, 57%), identical with that obtained in the pyrolysis of **5** in triethylene glycol.

$Na_2S_2O_4$ Reduction of 30.—A suspension of 1 g (3.1 mmol) of **30** in 50 ml of 80% ethanol, to which 1 g (6.3 mmol) of $Na_2S_2O_4$ had been added, was refluxed for 30 min; upon cooling, the yellow solid was filtered to yield 0.73 g (75%) of **15**.

5,12-Dihydrobenzo[*b*]phenazine (17) was prepared from *o*-phenylenediamine and 2,3-dihydroxynaphthalene in 68% yield:[19] darkened at 201–215° but did not melt below 400°; ir (KBr) 2.92 μ (NH); nmr (DMSO-d_6) δ 7.78–7.42 (m, 2, C-6 and C-11 hydrogens) 7.38–6.96 (m, 2, C-6 and C-11 hydrogens), 7.38–6.96 (m, 4, C-7, C-8, C-10 hydrogens), 6.74–6.26 (m, 4, C-1, C-2, C-3, and C-4 hydrogens), and 5.70 (broad mound, 2, NH, exchangeable with D_2O).

Benzo[*b*]phenazine (16), mp 231–232° (lit.[19] mp 233°), was obtained in 21% yield *via* the chromic acid oxidation of **17**.[19]

Pyrolysis of 6.—A suspension of **6** (1.0 g, 2.6 mmol) in 30 ml of diethylene glycol was refluxed (240°) for 3 hr. On cooling, the glycol solution was added to 100 ml of water and the resultant mixture was filtered. The solid material was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I) and eluted successively with hexane (100 ml), 1:1 hexane–ether (100 ml), and ether (200 ml). Evaporation of the hexane fraction gave a light yellow oil (0.1 g, 12%) which was spectrally identified as **2-(α-methylbenzyl)-3-benzylquinoxaline (22)**: uv max (95% EtOH) 240 mμ (ϵ 30,000), 311 sh (9500), and 321 (11,000); nmr (CCl_4) δ 7.85 (center of A_2B_2 multiplet, 4, quinoxaline), 7.18 (s, 10, C_6H_5), 4.49 (q, 1, J = 7 Hz, CH), 4.28 (s, 2, CH_2), and 1.65 (d, 3, J = 7 Hz, CH_3).

Evaporation of the hexane–ether fraction led to 0.19 g (22%) of **6-phenyl-11-methylbenzo[*b*]phenazine (23)** as red needles: mp 253–254° (from 1,2-dichloroethane); uv max (95% EtOH) 250 mμ (ϵ 51,000), 288 (94,500), and 322 (8500); nmr ($CDCl_3$) δ 8.50–7.20 (m, 8, C-1, C-2, C-3, C-4, C-6, C-7, C-8, and C-9 hydrogens), 7.50 (s, 5, C_6H_5), and 3.28 (s, 3, CH_3).

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74; mol wt, 320. Found: C, 86.45; H, 4.74; N, 8.81; mol wt, 350 (isothermal distillation).

Evaporation of the ether fraction produced 0.38 g (38%) of unreacted **6**.

Pyrolysis of 7.—A suspension of **7** (1.0 g, 2.5 mmol) in 30 ml of triethylene glycol was refluxed (280°) for 4 hr. On cooling, the glycol solution was added to 100 ml of water and the whole was extracted with two 100-ml portions of ether. The ether extracts were combined, dried (Na_2SO_4), and evaporated to a reddish oil which was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I). Elution of the column with 200 ml of pentane led, after evaporation of the solvent, to a clear oil which was dissolved in 50 ml of petroleum ether (bp 60–70°), charcoaled (Norit), and filtered, and the filtrate was reduced in volume to 20 ml. On standing, 0.11 g (14%) of an inseparable *meso–dl* mixture of **2,3-bis(α-methylbenzyl)quinoxaline (24)** deposited as white crystals: mp 89–90.5°; uv max (95% EtOH) 238 mμ (ϵ 38,000), 310 (10,000), and 321 (12,000); nmr ($CDCl_3$) δ 7.82 (center of A_2B_2 multiplet, 4, quinoxaline), 7.20 and 7.01 (each singlet, 10, *dl* and *meso* C_6H_5, respectively), 4.52 (m, 2, overlapping pair of quartets from *meso* and *dl* isomers), 1.76 and 1.54 (each doublet, 6, J = 7 Hz, *meso* and *dl* CH_3, respectively).

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28; mol wt, 338. Found: C, 84.88; H, 6.85; N, 8.36; mol wt, 326 (isothermal distillation).

Continued elution of the column with 100 ml of ether led ultimately to 0.05 g (4%) of **23** and recovery of 0.32 g (32%) of **7**.

Photolysis of 5.—A solution of **5** (1.0 g, 2.7 mmol) in 125 ml of dioxane (distilled from CaH_2), sensitized with 0.1 g of benzophenone, was irradiated (Vycor filter, >2200 Å; 125-W Hanovia medium pressure Hg arc) under N_2 for 48 hr during which the color changed from bright yellow to deep red. Evaporation of the solvent (Rinco) gave a dark red oil which was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I). Elution of the column with 250 ml of CCl_4, followed by evaporation of the eluate (Rinco), left a light pink oil which slowly solidified on standing to give 0.19 g (22%) of **2,3-dibenzylquinoxaline (12)**, mp 118–118.5°.

Continued elution of the column with CH_2Cl_2, $CHCl_3$, and ether resulted only in the isolation of tars which could not be further characterized.

Alkaline Hydrogen Peroxide Oxidation of 5.—A suspension of **5** (1.0 g, 2.7 mmol) in 30 ml of 95% ethanol, 5 ml of 30–35% hydrogen peroxide, and 5 ml of 2 *N* sodium hydroxide was heated on a steam bath with stirring for 20 min. The dark red solution slowly faded during the vigorous reaction and a tan crystalline solid appeared. The mixture was cooled, diluted with 50 ml of water, and filtered to yield 0.75 g (85%) of crude **2-benzyl-3-benzoylquinoxaline (11)**. Recrystallization from hexane (Norit) gave pure **11** as white chunky crystals: mp 96–96.5°; ir (KBr) 5.99 and 6.02 μ (C=O); uv max (95% EtOH) 230 mμ (ϵ 17,000), 259 (21,700), and 326 (11,300); nmr ($CDCl_3$) δ 8.30–7.10 (m, 14, aromatic) and 4.60 (s, 2, CH_2).

Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.46; mol wt, 324. Found: C, 81.48; H, 4.93; N, 8.52; mol wt, 326 (Rast).

Alkaline Hydrogen Peroxide Oxidation of 6.—To a solution of 1 g (2.6 mmol) of **6** in 30 ml of 95% ethanol was added 5 ml of 30–35% hydrogen peroxide and 5 ml of 2 *N* NaOH. The mixture was heated on a steam bath for 20 min, until the vigorous reaction had subsided and the solution turned a light yellow. The solution was cooled and added to 100 ml of ice water. The aqueous solution was extracted with two 100-ml portions of pentane. The combined pentane extracts were dried (Na_2SO_4), treated with Norit, and filtered, and the filtrate was reduced in volume to 20 ml. On standing, a white crystalline solid appeared which was filtered to give 0.64 g (69%) of **2-(α-methylbenzyl)-3-benzoylquinoxaline (31)**, as tiny white needles: mp 77.5–78.5° (from pentane); ir (KBr) 6.01 μ (C=O); uv max (95% EtOH) 246 mμ (ϵ 38,000) and 323 (9000); nmr ($CDCl_3$) δ 8.35–7.20 (m, 14, aromatic), 4.94 (q, 1, J = 7 Hz, CH), and 1.86 (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.46; H, 5.36; N, 8.28; mol wt, 338. Found: C, 81.64; H, 5.50; N, 8.37; mol wt, 330 (Rast).

Alternatively, **31** was prepared in 10% yield by methylation (CH_3I) of **11** in dry *t*-BuOH in the presence of KO-*t*-Bu.

Sodium Borohydride–Methanol Reduction of 5 and 6.—Sodium borohydride (1.0 g, 0.026 mol) was added in small portions of 1 g of **5** suspended in 50 ml of warm (steam bath) absolute methanol. The first addition of $NaBH_4$ led to a vigorous reaction and a transient orange color which darkened on further addition. After addition was complete, the solution was filtered to remove unreacted starting material. On cooling, the color of the dark red filtrate faded to yellow and a white crystalline solid [$NaB(OCH_3)_4$] appeared. Distilled water (100 ml) was added and the solution was extracted with two 100-ml portions of pentane. The combined pentane extracts were dried (Na_2SO_4) and evaporated to a light pink oil. The oil was redissolved in 50 ml of pentane, treated with Norit, filtered, and cooled to yield 0.62 g (74%) of **2,3-dibenzylquinoxaline (12)**.

Similar addition of 1.0 g of $NaBH_4$ in portions to 1.0 g of **6** in 50 ml of absolute CH_3OH also led to a vigorous reaction. After addition was complete, the solution was heated for an additional 10 min and filtered. Distilled water was added and the aqueous solution was extracted with two 100-ml portions of pentane.

The combined pentane extracts were dried (Na_2SO_4), filtered and evaporated to dryness (Rinco) to give 0.33 g (29%) of **22**.

Preparation of 2,3-Dibenzoylquinoxaline (27).—A solution of 2-benzyl-3-benzoylquinoxaline **11** (1.0 g, 3.1 mmol) in 30 ml of glacial HOAc and 0.5 g (5 mmol) of CrO_3 in 10 ml of 50% acetic acid was heated on a steam bath for 10 min, and then added to 150 ml of an ice–water mixture. The resultant light green solid was filtered and dried to yield 0.97 g (93%) of **27**, as a white powder: mp 169–170° (from methanol, Norit); ir (KBr) 6.03 μ (C=O); uv max (95% EtOH) 257 mμ (ϵ 48,000) and 324 (8000); nmr (DMSO-d_6) δ 8.35–7.30 (m, aromatic).

Anal. Calcd for $C_{22}H_{14}N_2O_2$: C, 78.09; H, 4.17; N, 8.28; mol wt, 338. Found: C, 78.01; H, 4.31; N, 8.12; mol wt, 350 (Rast).

Preparation of 1,4-Diphenyl-2,3-diazaphenazine (28).—A solution of 1.0 g (2.96 mmol) of **27** in 30 ml of ethylene glycol was refluxed for 4 hr at 180–200° in the presence of 0.33 g (5.9 mmol) of solid KOH and 3 ml of 85% hydrazine hydrate. After cooling, the reaction mixture was diluted with 150 ml of distilled water and then filtered. The filtrate was extracted with two 100-ml portions of pentane; evaporation to dryness of the combined pentane extracts gave 2,3-dibenzylquinoxaline (**12**) in 2% yield.

The insoluble material, originally filtered, was dissolved in 200 ml of methanol, heated with charcoal (Norit), filtered, and evaporated to 50 ml. On cooling, 0.44 g (43%) of **28** crystallized as pale yellow needles: mp 239–240.5° (from CH_3OH, Norit); uv max (95% EtOH) 245 mμ (ϵ 62,000), 274 sh (20,000) and 345 (7000); nmr ($CDCl_3$)[50] δ 8.43 (m, 4, *ortho* hydrogens of C_6H_5), 8.15 (center of A_2B_2 pattern, 4, C-6, C-7, C-8, and C-9 hydrogens), and 7.60 (m, 6, *meta* and *para* hydrogens of C_6H_5).

Anal. Calcd for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.75; mol wt, 336. Found: C, 79.18; H, 4.37; N, 16.48.

Preparation of 2-(α-Bromobenzyl)-3-benzoylquinoxaline (32).—A suspension of 2.0 g (6.2 mmol) of **11** and 1.1 g (6.2 mmol) of NBS in 100 ml of CCl_4 was irradiated with a 225 W high intensity white light for 1 hr. The mixture was cooled, filtered to remove the precipitated succinimide (0.62 g), and then evaporated *in vacuo* to a light green oil which was deposited on a 2.5 × 25 cm column of Woelm alumina (neutral, activity grade I) and eluted with 250 ml of 1:1 hexane–ether. The eluate was treated with charcoal (Norit), filtered, and evaporated to 50 ml. On cooling, 1.20 g (48%) of **32** was obtained as light green needles: mp 91–92.5° (from hexane); ir (KBr) 6.01 μ (C=O); uv max (95% EtOH) 254 mμ (ϵ 32,000) and 327 (6400); nmr ($CDCl_3$) δ 8.30–7.20 (m, 14, aromatic) and 6.96 (s, 1, CH).

Anal. Calcd for $C_{22}H_{15}N_2OBr$: C, 65.52; H, 3.75; N, 6.94; mol wt, 403. Found: C, 65.32; H, 3.67; N, 7.15; mol wt, 387 (isothermal distillation).

Compound **32** was unstable to light and heat and slowly decomposed to a gray powder.

Preparation of 2-(α-Hydroxybenzyl)-3-benzylquinoxaline (34).—To a solution of 1.0 g (3.1 mmol) of **11** in 30 ml of 95% ethanol was added a solution of 0.16 g (4.2 mmol) of $NaBH_4$ and 2 ml of 2 *N* NaOH in 10 ml of 95% EtOH, and the whole was refluxed 1 hr. On cooling, the mixture was added to 50 ml of ice–water and neutralized (litmus) with 10% HCl. The aqueous solution was extracted with two 100-ml portions of pentane. The combined pentane extracts were dried (Na_2SO_4), treated with charcoal (Norit), filtered, and evaporated to 50 ml. On standing, the white flocculent solid was filtered to yield 0.76 g (75%) of **34**: mp 83–84.5°; ir (KBr) 3.25 and 3.30 μ (OH); uv max (95% EtOH) 240 mμ (ϵ 29,500), 311 sh (7800), and 321 (10,000); nmr ($CDCl_3$) δ 8.22–7.50 (m, 4, quinoxaline), 7.47–7.03 (m, 10, C_6H_5), 5.88 (s, 1, CH), 5.20 (broad singlet, 1, OH exchangeable with D_2O), and 4.16 (s, 2, CH_2).

Anal. Calcd for $C_{22}H_{18}N_2O$: C, 80.95; H, 5.58; N, 8.58; mol wt, 326. Found: C, 81.84; H, 5.73; N, 8.76; mol wt, 330 (isothermal distillation).

All attempts to prepare the tosylate of **34** were unsuccessful.

Cyclodehydration Reactions.—The general procedure for this reaction was as follows. The appropriate quinoxaline (1.0 g) was treated with 5 ml of concentrated H_2SO_4 and warmed briefly on a steam bath (5 min for **11** and **34**; 30 min for **31** and **32**). The cooled solution was added to 100 g of ice, and the aqueous solution was extracted with two 100-ml portions of CH_2Cl_2. The methylene chloride extracts were dried (Na_2SO_4), filtered, and evaporated to dryness to yield the crude benzo[*b*]phenazine product. Thus **11** and **34** gave, respectively, 0.81 g (85%) and 0.54 g (62%) of **6-phenylbenzo[*b*]phenazine (13)**, mp 254–255° (from 1,2-dichloroethane).

2-(α-Methylbenzyl)-3-benzoylquinoxaline (31) gave 0.75 g (78%) of **6-phenyl-11-methylbenzo[*b*]phenazine (23)**, as red needles: mp 253–254° (from 1,2-dichloroethane, Norit); uv max (95% EtOH) 250 mμ (ϵ 51,000), 288 (94,500), and 322 (8500); nmr ($CDCl_3$) δ 8.50–7.20 (m, 8, C-1, C-2, C-3, C-4, C-7, C-8, C-9, and C-10 hydrogens), 7.50 (s, 5, C_6H_5), and 3.28 (s, 3, CH_3).

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74; mol wt, 320. Found: C, 86.45; H, 4.74; N, 8.81; mol wt, 350 (isothermal distillation).

2-(α-Bromobenzyl)-3-benzoylquinoxaline (32) gave 0.81 g (84%) of **6-phenyl-11-bromobenzo[*b*]phenazine (33)**, as red needles: mp 263–264° (from CH_2Cl_2, Norit); uv max (95% EtOH) 254 mμ (ϵ 40,000) and 288 (87,500); nmr[51] ($CDCl_3$) δ 8.72 (m, 1, C-10 hydrogen), 8.35 (m, 1, C-7 hydrogen), 8.20–7.10 (m, 6, C-1, C-2, C-3, C-4, C-8, and C-9 hydrogens), and 7.57 (s, 5, C_6H_5).

Anal. Calcd for $C_{22}H_{13}N_2Br$: C, 68.57; H, 3.40; N, 7.27; mol wt, 385. Found: C, 68.74; H, 3.25; N, 7.05; mol wt, 400 (isothermal distillation).

Peroxy Acid Oxidation of 5.—A mixture of 2.0 g (5.4 mmol) of **5** and 2.5 g (14 mmol) of *m*-chloroperbenzoic acid in 125 ml of $CHCl_3$ was refluxed for 2 hr. The clear amber solution was reduced in volume to 50 ml (Rinco) and cooled. The precipitated *m*-chlorobenzoic acid was filtered, and the filtrate was evaporated to a dark yellow-brown oil, which solidified on standing to yield 0.86 g (47%) of crude **2-benzyl-3-benzoylquinoxaline 1-oxide (29)**. Recrystallization from 95% ethanol (Norit) gave pure **29** as yellow needles: mp 139–140°; ir (KBr) 6.01 μ (C=O); uv max (95% EtOH) 243 mμ (ϵ 32,500), 248 (26,000), 276 (14,500), and 326 (7300); nmr ($CDCl_3$) δ 8.68 (m, 1, C-8 hydrogen), 8.4–7.0 (m, 13, aromatic), and 4.52 (s, 2, CH_2).

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.64; H, 4.70; N, 8.23; mol wt, 340. Found: C, 77.78; H, 4.83; N, 8.30; mol wt, 350 (Rast).

Sodium Hydrosulfite Reduction of 29.—A mixture of **29** (0.45 g, 1.3 mmol) and sodium hydrosulfite (0.25 g, 1.6 mmol) in 25 ml of 80% EtOH was refluxed for 1 hr. The resultant deep purple solution was added to 20 ml of ice and the aqueous solution was extracted twice with 50-ml portions of ether. The combined ether extracts were dried (Na_2SO_4), filtered, treated with charcoal (Norit), and again filtered. Evaporation of the filtrate to dryness gave 0.38 g (90%) of **11**, mp 96–97°, identical by all the usual criteria with **11** prepared by the oxidation of **5** with alkaline hydrogen peroxide.

Oxidation of **11** with peracetic acid (40%) in chloroform (reflux, 2 hr) gave a 76% yield of **29**.

6-Phenylbenzo[*b*]phenazine 12-Oxide (30). *Via* Cyclodehydration of 29.—2-Benzyl-3-benzoylquinoxaline 1-oxide (**29**, 1.0 g, 2.9 mmol) in 5 ml of concentrated H_2SO_4 was warmed on a steam bath for 10 min. Work-up was identical with that employed in the cyclization of **11**, **31**, **32**, and **34**. Crude **6-phenylbenzo[*b*]phenazine 12-oxide (30)** was obtained as a red powder from CH_2Cl_2 and deposited on a 2.5 × 25 cm column of Florisil (60–200 mesh). Elution with CH_2Cl_2 resulted in the development of two red bands. Evaporation of the first 150 ml of eluent gave **30** (0.62 g, 66%) as dark red plates: mp 248–249.5° (from 1,2-dichloroethane); uv max (95% EtOH) 244 mμ (ϵ 16,000), 242 (36,000), and 286 (77,500); nmr[51] ($CDCl_3$) δ 9.35 (s, 1, C-11 hydrogen), 8.66 (m, 1, C-1 hydrogen), 8.25–7.30 (m, 7, quinoxaline), and 7.60 (s, 5, C_6H_5).

Anal. Calcd for $C_{22}H_{14}N_2O$: C, 81.97; H, 4.38; N, 8.69; mol wt, 322. Found: C, 81.72; H, 4.36; N, 8.45; mol wt, 320 (Rast).

Via Peracetic Acid Oxidation of 13.—The two-layer suspension of **13** in 30 ml of 1,2-dichloroethane and 5 ml of 40% peracetic acid was refluxed for 4 hr. The cooled mixture was added to 100 ml of ice–water and the whole was extracted with 100 ml of CH_2Cl_2. The organic extracts were washed successively with two 50-ml portions of water, 50 ml of 10% $NaHCO_3$ solution, and 50 ml of distilled water and then dried (Na_2SO_4). Filtration, followed by evaporation *in vacuo* to dryness, gave 0.65 g (67%) of **30**.

Bromination of 5.—One gram (2.7 mmol) of **5** and 0.5 g (2.8

(51) We are grateful to William Jankowski, Varian Associates, for determining the 100-Mc nmr spectrum of this compound, using a CAT.

mmol) of NBS were suspended in 125 ml of carbon tetrachloride and irradiated with a 225-W high intensity white light for 30 min. The suspension was cooled and filtered. The volume of the filtrate was reduced to 50 ml (steam bath) and the solution was again cooled and filtered. Final evaporation of the filtrate *in vacuo* left a light tan oil which solidified, with darkening, to give 0.67 g (58%) of crude **1,3-diphenyl-1-bromo-1,3-dihydrothieno-[3,4-*b*]quinoxaline 2,2-dioxide.** Recrystallization from chloroform gave the monobromo product as a light yellow, heat-sensitive, crystalline solid: darkened at 130°, mp 230–232° dec; uv max (95% EtOH) 248 mμ (ε 28,000), 279 sh (10,000) and 326 (7200); nmr ($CDCl_3$) δ 8.25–7.20 (m, 14, aromatic) and 6.15 (s, 1, CH).

Bromination of 11.—A solution of 0.25 g (0.81 mmol) of **11** and 0.30 g (1.7 mmol) of NBS in 25 ml of CCl_4 was refluxed for 2 hr. On cooling, the succinimide was filtered, and the filtrate was evaporated to leave a pink oil which solidified to give 0.21 g (63%) of a mixture of *meso*- and *dl*-**2,3-*bis*(α-bromobenzyl)-quinoxaline** (**42**) as pale pink needles: mp 163–165° (from hexane); uv max (95% EtOH) 247 mμ (ε 29,000) and 329 (6500); nmr (CCl_4) δ 8.17–7.08 (m, 14, aromatic) and 6.64 (*meso*) and 6.48 (*dl*) (each singlet, 2, CH).

Anal. Calcd for $C_{22}H_{16}N_2Br_2$: C, 56.54; H, 3.45; N, 7.21. Found: C, 56.54; H, 3.65; N, 7.05.

Registry No.—Sulfur dioxide, 7446-09-5; **5**, 19029-25-5; *cis* **7**, 19029-79-9; *trans* **7**, 19029-80-2; **9**, 19029-26-6; **10**, 19029-27-7; **11**, 19029-28-8; **13**, 19029-29-9; **14**, 19029-30-2; **15**, 19029-31-3; **17**, 19029-32-4; **22**, 19029-33-5; **23**, 19029-34-6; *meso* **24**, 19029-81-3; *dl* **24**, 19029-82-4; **27**, 19029-35-7; **28**, 19029-36-8; **29**, 19029-37-9; **30**, 19029-38-0; **31**, 19029-39-1; **32**, 19029-40-4; **33**, 19029-41-5; **34**, 19029-42-6; *meso* **42**, 19029-83-5; *dl* **42**, 19029-84-6; 1,3-diphenyl-1-bromo-1,3-dihydrothieno[3,4-*b*]-quinoxaline 2,2-dioxide, 19029-43-7.

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Preparation and Reactions of *o*-(Cyanomethyl)benzeneboronic Acid[1]

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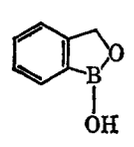
The synthesis of *o*-(cyanomethyl)benzeneboronic acid **3** is described. Conversion of the nitrile to the amide, acid, alcohol, and amine and cyclodehydration of these substances yield, respectively, the cyclic imide of *o*-boronophenylacetic acid **4**, the cyclic anhydride of *o*-boronophenylacetic acid **5**, the lactone of 2-(*o*-boronophenyl)-ethanol **15** and the lactam of 2-(*o*-boronophenyl)ethylamine **18**. The reaction of cyclic imide **4** and cyclic anhydride **5** with catechol is reported, as is the reaction of **5** with *o*-aminophenol and *o*-phenylenediamine. The ease with which *ortho*-substituted arylboronic acids undergo cyclodehydration and further dehydration to dimeric anhydrides is discussed.

Alkaline hydrolysis of *o*-(bromomethyl)benzeneboronic acid yields boronophthalide **1**,[2,3] the lactone of *o*-(hydroxymethyl)benzeneboronic acid. This lactone is more stable than would be predicted on the basis of the chemistry of simple boronic esters.[3–5] Similarly, reaction of *o*-formylbenzeneboronic acid with hydroxylamine gives a cyclic product **2**.[3,6,7] It seems likely that additional compounds analogous to **1** and **2** will result from the interaction of an aromatic boronic acid group and a second function suitably located on a side chain in the *ortho* position. *o*-(Cyanomethyl)benzeneboronic acid (**3**) should be a useful precursor for such substances because of the ease with which a nitrile group can be converted into other reactive functions.



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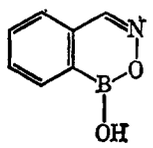

2

Lennarz,[8] in attempts to displace the bromide atom of *o*-(bromomethyl)benzeneboronic anhydride with cyanide, employing strongly basic cyanides and various solvent systems, observed only the formation of boronophthalide **1**. In the present work replacement of the bromine atom is effected when *o*-(bromomethyl)-benzeneboronic anhydride reacts with cyanide ion introduced as the ion associated with a strongly basic ion-exchange resin. The general method is one introduced by Griffin, *et al.*,[9] as a means of avoiding undesirable base-promoted processes brought about by alkali cyanides.

Hydrolysis of *o*-(cyanomethyl)benzeneboronic acid (**3**) with dilute base gives cyclic imide **4** which is further hydrolyzed in acid to cyclic anhydride **5**; neither *o*-(boronophenyl)acetamide nor *o*-(boronophenyl)acetic

(1) This work was supported by Grant AT(11-1)-314 from the Atomic Energy Commission, Report No. C00-314-13.

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