Phenylfurazan Oxide. Structure

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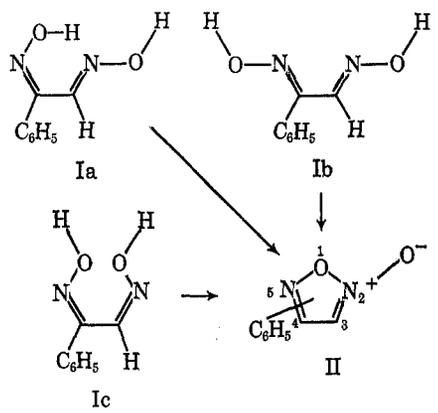
Three isomers of phenylglyoxime have been oxidized to the same phenylfurazan oxide in separate reactions. The 4-phenylfurazan 2-oxide structure has been assigned to the product on the basis of nmr spectroscopic arguments. Isomerization of 4-phenylfurazan 2-oxide into 3-phenylfurazan 2-oxide was not observed although an equilibrium between the two is possible.

Phenylfurazan oxide is readily synthesized by oxidation of phenylglyoxime by dinitrogen tetroxide.[1] Two structures can be written for the product, 3-phenylfurazan 2-oxide (IIa) or 4-phenylfurazan 2-oxide (IIb).



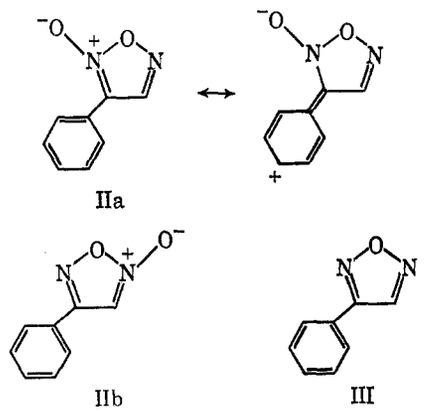
Ia Ib Ic II

An equilibrium between isomeric furazan oxides has been demonstrated in disubstituted furazan oxides and benzofurazan oxides.[2] The equilibration presumably involves the corresponding dinitroso intermediates. Thus, there was the possibility that phenylfurazan oxide existed as a mixture of IIa and IIb.

Reports claim the isolation of two phenylfurazan oxides by separate oxidation of two isomers of phenylglyoxime,[1] but characterization centered on small differences in melting point, 108° *vs.* 111°, and structures were not firmly assigned. Three isomers of phenylglyoxime have now been isolated. The physical constants of each of the pure isomers were not in agreement with those reported for the phenylglyoxime isomers used in previous syntheses of phenylfurazan oxide.[3] It would appear that the previous studies of phenylfurazan oxide involved oxidation of mixtures of phenylglyoxime isomers. In this work, the presence of two isomers of phenylfurazan *N*-oxide was not observed even though three isomers of phenylglyoxime were oxidized in separate reactions.

Nmr measurements at varied temperature have been used to demonstrate equilibration in furazan oxides.[2] Nmr spectroscopy was used in the present work to show the lack of detectable equilibrium in phenylfurazan oxide and to determine that the compound exists as 4-phenylfurazan 2-oxide (IIb).

A firm prediction as to the correct structure of phenylfurazan oxide could not be made *a priori*. 3-Phenylfurazan 2-oxide (IIa) may be stabilized by facile charge delocalization into the phenyl ring. Such is not the case with 4-phenylfurazan 2-oxide (IIb). However, IIa has an unfavorable stereochemical interaction between the phenyl group and the oxide; this interaction is missing in IIb. It was not clear which factor would predominate.



IIa IIb III

Results and Discussion

The same phenylfurazan oxide (II) was synthesized from each of three phenylglyoxime isomers (Ia–Ic) by oxidation with dinitrogen tetroxide in ether.[1] The reaction proceeded smoothly with *anti*-phenyl-*amphi*-glyoxime (Ia) and phenyl-*syn*-glyoxime (Ic), whereas impurities were observed when phenyl-*anti*-glyoxime (Ib) was oxidized. The isomers can yield the same product by isomerization before reaction in the acidic reaction medium. The impurities observed in the reaction with phenyl-*anti*-glyoxime (Ib) appeared to be nitro derivatives as detected in infrared spectral measurement. Nitro compounds are known products of reaction between oximes and dinitrogen tetroxide.[4]

The products of these oxidations were crystalline solids, melting over two degrees in the 105–110° range. Recrystallization from *m*-xylene raised the melting points to 108–110° (usually reported[1]) without change in ir or nmr spectra. Phenylfurazan oxide was found to be stable at its melting point since the resolidified melt showed no change in its ir spectrum.[5] Table I and Figure I contain nmr and mass spectral data on II and III.

The mass spectrum of phenylfurazan oxide is readily interpretable (Table I). It is questionable whether or

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(1) For reviews on phenylfurazan oxide, see "Beilstein's Handbuch der Organischen Chemie," 4th ed, Vol. XXVII, B. Prager, P. Jacobsen, and F. Richter, Ed., Springer Verlag, Berlin, 1937, p 575; 2nd suppl, F. Richter, Ed., 1955, pp 632–633. J. S. Michelman, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1965. K. L. Hill, U. S. Patent 3,410,676 (1968).

(2) P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, **45**, 504 (1962); F. B. Mallory and A. Cammarata, *J. Amer. Chem. Soc.*, **88**, 61 (1960).

(3) J. V. Burakevich, A. M. Lore, and G. P. Volpp, *J. Org. Chem.*, **35**, 1 (1970).

(4) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, pp 57–58.

(5) For data on the ir absorption of furazan oxides, see J. H. Boyer, D. I. McCane, W. J. McCarville, and A. T. Tweedie, *J. Amer. Chem. Soc.*, **75**, 5298 (1953); N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *ibid.*, **77**, 4238 (1955).

TABLE I
SPECTRAL DATA COLLECTED ON PHENYLFURAZAN OXIDE, PHENYLFURAZAN, AND FURAZAN

Compd	Nmr (CCl_4), δ, ppm	Nmr ($CDCl_3$), δ, ppm	Mass spectrum *m/e* (rel intensity), assignment
4-Phenylfurazan 2-oxide (IIb)	7.13 [s, 1, -C(=N-)H] 7.62 (m, 5, phenyl)	7.26 [s, 1, -C(=N-)H] 7.60 (m, 5, phenyl)	162 (15), M^+ 146 (6.0), $M^+ - O$ 145 (2.0), $M^+ - OH$ 132 (14), $M^+ - NO$ 103 (44), $C_6H_5CN^+$ 102 (100), $C_6H_5C{\equiv}CH^+$
Phenylfurazan[a] (III)	8.42 [s, 1, -C(=N-)H] 7.83 (m, 2, phenyl) 7.48 (m, 3, phenyl)	8.60 [s, 1, -C(=N-)H] 7.83 (m, 2, phenyl) 7.54 (m, 3, phenyl)	146 (56), M^+ 119 (100), $C_6H_5CNO^+$ 116 (38), $M^+ - NO$ 103 (46), $C_6H_5CN^+$
Furazan[a] (VI)	8.19		

[a] See ref 9.

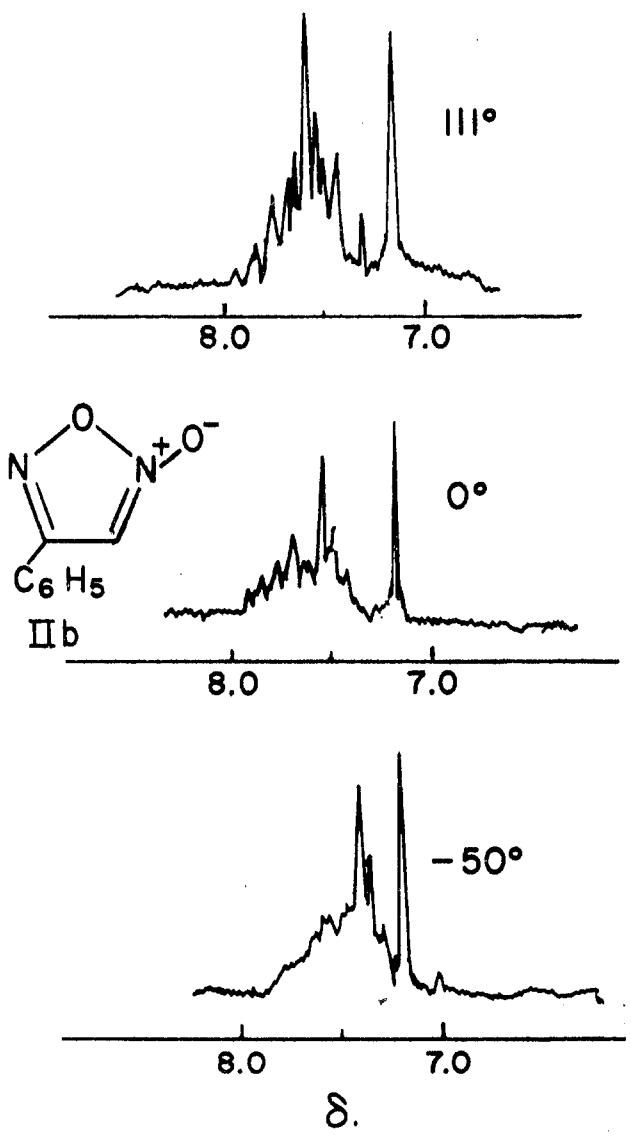
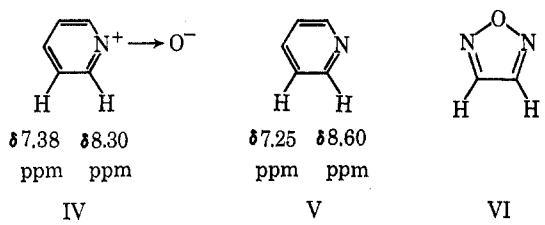


Figure 1.—Nmr spectra of phenylfurazan oxide in chloroform-*d* solution at various temperatures.

not the small $(M - 17)^+$ ion indicating loss of -OH in the fragmentation can be associated with the structure of the parent phenylfurazan oxide although it did suggest the 4-phenylfurazan 2-oxide structure in agreement with the conclusion reached from nmr considerations.

The nmr spectrum of phenylfurazan *N*-oxide (Figure 1) showed the phenyl protons as a multiplet and the lone heterocyclic ring proton as a singlet. Thus, the nmr integration indicates that only one isomer was present. The positions of the nmr signals of phenylfurazan oxide (II) and phenylfurazan (III) listed in Table I were found to be concentration independent in both carbon tetrachloride and chloroform-*d* solutions 0.2 *M* or less. The difference in chemical shift between the protons on the heterocyclic rings in phenylfurazan oxide and phenylfurazan was used to determine structure.

The proton on the heterocyclic ring in phenylfurazan oxide appears at much higher field than that in phenylfurazan in at least two solvents (Table I). *N*-Oxide groups shield protons located on the α-carbon atoms relative to those in the corresponding base, as seen by comparison of the nmr values reported for pyridine *N*-oxide (IV) and pyridine (V)[6] given on the structural drawings. In the present study, it was shown that these values are concentration independent in chloroform in solutions 0.2 *M* or less. The nmr data, therefore, indicate that phenylfurazan *N*-oxide exists as 4-phenylfurazan 2-oxide.



IV V VI

The large differences in chemical shift between the heterocyclic protons of II and III (1.29 ppm in carbon tetrachloride and 1.34 ppm in chloroform) eliminate the possibility that phenylfurazan *N*-oxide exists as 3-phenylfurazan 2-oxide. These large upfield shifts cannot result from diamagnetic shielding by the phenyl group rotated out of planarity with the heterocyclic ring through steric interaction with the *N*-oxide. Such shifts would arise from the elimination of deshielding caused by coplanarity of the heterocyclic ring proton and the phenyl group (0.23 ppm, compare III and VI in Table I) and shielding of this proton by the phenyl group when the rings are orthogonal (0.2 ppm, estimated from Dreiding Molecular Models and the dia-

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates (National Press), U. S. A., 1962, spectrum 96; P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **4**, 1393 (1965).

gram of Johnson and Bovey[7]). Thus, under such conditions, the maximum upfield shift would be predicted to be only about 0.5 ppm in contrast to the observed shifts of 1.29 and 1.34 ppm. Another argument against this situation is that orthogonality of the rings would prevent charge delocalization, the favorable factor present in 3-phenylfurazan 2-oxide when compared to 4-phenylfurazan 2-oxide.

Only minor variations were observed in the nmr spectra of 4-phenylfurazan 2-oxide at high and low temperature (Figure 1). The small peak at δ 7.0 ppm in the spectrum at $-50°$ presumably arises from rotamer fixation and not from isomerization which should produce a downfield shift, not an upfield one. The peak at δ 7.3 ppm in the spectrum at 111° is suspiciously close to chloroform solvent resonance. At temperatures higher than 111°, the nmr solution turned into a gel.[8]

The phenylfurazan used in the nmr study was synthesized by dehydration of phenylglyoxime.[9] The spectral data collected on it appear in Table I. The mass spectrum of phenylfurazan can be interpreted according to the fragmentation pattern previously recorded for furazans.[10]

Experimental Section[8,11]

4-Phenylfurazan 2-Oxide from *anti*-Phenyl-*amphi*-glyoxime.[1,3]—An ice-cooled solution of 2 g of *anti*-phenyl-*amphi*-glyoxime (Ia)[3] in 20 ml of anhydrous ether was treated with gaseous dinitrogen tetroxide until a green-colored solution resulted. The ice bath was removed and the solution was concentrated by passing a stream of nitrogen over it. The precipitated II was removed by filtration as a white powder (1.4 g, 71% yield): mp 108–110°; ir spectrum ($CHCl_3$) 3165 (w), 1610 (s), 1603 (m), 1471 (w), 1451 (m), 1399 (m), 1182 (w), 1000 (w), 985 (w), and 935 cm^{-1} (w). The nmr spectrum is reproduced in Figure 1.[5]

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.41; H, 4.01; N, 17.02.

A stream of nitrogen was then used to completely remove the solvent from the filtrate obtained during the isolation of the above product. The infrared and nmr spectra of the residue were virtually the same as the pure product.

4-Phenylfurazan 2-Oxide from Phenyl-*anti*-glyoxime.[1,3]—Dinitrogen tetroxide gas was passed into an ice-cooled solution of 2 g of phenyl-*anti*-glyoxime (Ib)[3] in 75 ml of anhydrous ether for 15 min. A stream of nitrogen was then used to evaporate solvent from the reaction mixture to near dryness. The precipitate that formed was collected by filtration, yield 800 mg (40% yield), mp 98–102°. The infrared and nmr spectra of samples isolated at this point were essentially superimposable upon those of the product of oxidation of *anti*-phenyl-*amphi*-glyoxime (see above). Only minor extraneous peaks resulting from impurities were observed. Recrystallization of the crude product first from *m*-xylene and then from *m*-xylene–petroleum ether (bp 30–60°) afforded 200 mg of 4-phenylfurazan 2-oxide, mp 106–108°.

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.02; H, 3.76; N, 16.84.

Further evaporation of the solvent from the reaction mother liquor gave a residue whose ir spectrum was complex in the region 1689–1346 cm^{-1}. The spectrum suggested the presence of nitro derivatives which are known to be products of reaction between oximes and dinitrogen tetroxide.[4]

4-Phenylfurazan 2-Oxide from Phenyl-*syn*-glyoxime.[1,3]—The synthesis was accomplished by following the procedure outlined above in the oxidation of *anti*-phenyl-*amphi*-glyoxime but with use of a solution of 200 mg of phenyl-*syn*-glyoxime (Ic)[3] in 10 ml of anhydrous ether. A white powder was obtained, 50 mg (25% yield), mp 105–107°. The infrared and nmr spectra were the same as obtained from the product of oxidation of *anti*-phenyl-*amphi*-glyoxime (see above).

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.50; H, 3.99; N, 17.06.

Here, also, a stream of nitrogen was used to completely remove the solvent from the filtrate obtained during the isolation of the pure product. Again, the infrared and nmr spectra of the residue were virtually the same as the pure product.

Registry No.—IIb, 7707-64-4.

(7) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 95.

(8) The nmr spectra of phenylfurazan oxide at low temperatures were determined by Dr. G. Dudek, Department of Chemistry, at Harvard University on a Varian A60 instrument equipped with a variable temperature probe. The high temperature nmr spectra were determined by Dr. S. Young at FMC Corp., Niagara Division, on a similar instrument. The authors wish to thank them for their kind cooperation.

(9) R. A. Olofson and J. S. Michelman, *J. Org. Chem.*, **30**, 1854 (1965).

(10) H. E. Ungnade and E. D. Loughran, *J. Heterocycl. Chem.*, **1**, 61 (1964).

(11) All melting points were determined with a Mettler FP1 melting point apparatus equipped with a Bausch and Lomb VOM 5 recorder. Infrared spectra were recorded on a Perkin-Elmer 421 grating spectrophotometer. A Varian A-60 spectrometer was used to obtain the nmr spectra at room temperature and tetramethylsilane was used as the internal standard. The mass spectra were determined on a Consolidated Electrodynamics Corporation Model 21-103C spectrometer.