mp 387 °C), whose IR spectrum is fully consistent with that of authentic specimen.[23c]

A mixture of 188 mg (0.5 mmol) of **12** and 561 mg (5 mmol) of potassium *tert*-butoxide in 20 mL of *tert*-butyl alcohol was refluxed for 1.5 h under nitrogen. The resulting mixture was treated as described above to give **3** (5%), **18** (27%), and **20** (36%).

(ii) In Tetrahydrofuran. To a stirred solution of potassium *tert*-butoxide (65 mg, 0.58 mmol) in anhydrous THF (18 mL) was added a solution of **12** (109 mg, 0.29 mmol) in 5 mL of THF at −15 °C. The mixture was gradually warmed to room temperature and stirred for additional 18 h. The solvent was removed under reduced pressure, and the residue was partitioned between dichloromethane and water. The dichloromethane layer was separated, washed with water, dried, and evaporated. Column chromatography of the residue gave **18** (5%), **20** (26%), and the starting material (yield was not determined).

(iii) In Dimethyl Sulfoxide. A mixture of 188 mg (0.5 mmol) of **12** and 561 mg (5 mmol) of potassium *tert*-butoxide in 20 mL of anhydrous Me_2SO was stirred for 18 h at room temperature under nitrogen. The resulting dark brown mixture was partitioned between dichloromethane (150 mL) and water (100 mL). The dichloromethane layer was separated, washed with water, dried, and evaporated to leave 28 mg of a brown oil, from which no pure product could be obtained by column chromatography.

(d) Butyllithium as Base. A solution of butyllithium in hexane (5 mmol) was added to a stirred solution of **12** (0.5 mmol) in 20 mL of anhydrous THF under nitrogen. The mildly exothermic reaction occurred. After being allowed to stand overnight, the mixture was quenched with water and evaporated to dryness. The residue was taken up in dichloromethane, washed with water, dried, and evaporated. Analysis of the residue TLC showed the presence of at least five products. Chromatographic purification did not given any pure identified product.

Reaction of 18 and 20 with Potassium *tert*-Butoxide. A mixture of 152 mg (1 mmol) of acenaphthylene (**18**) and 1.12 g (10 mmol) of potassium *tert*-butoxide in 40 mL of anhydrous *tert*-butyl alcohol was refluxed for 1.5 h. Treatment of the mixture gave **18** quantitatively. The formation of **3** was not observed at all.

A mixture of 231 mg (1 mmol) of 1-bromoacenaphthylene (**20**) and 1.12 g (10 mmol) of potassium *tert*-butoxide in 40 mL of *tert*-butyl alcohol was refluxed for 1.5 h. Compound **20** was recovered quantitatively, and formation of **3** was not observed.

Ramberg–Bäcklund Reaction of 12 in the Presence of Furan. A mixture of **12** (188 mg, 0.5 mmol), potassium *tert*-butoxide (561 mg, 5 mmol), and furan (2 mL) in anhydrous *tert*-butyl alcohol (20 mL) was stirred for 23.5 h at room temperature under nitrogen. The resulting yellow mixture was partitioned between dichloromethane (150 mL) and water (100 mL). The dichloromethane layer was separated, washed with water, dried, and evaporated. Purification of the residue by column chromatography afforded **3** (7%), **18** (10%), and **20** (19%). Adduct of furan with acenaphthyne was not obtained.

Oxidation of Acenaphthenequinone Dihydrazone (22) with Lead Tetraacetate. To a stirred suspension of **22**[4,24] in 100 mL of dichloromethane was added a solution of 4.88 g (11 mmol) of lead tetraacetate in 20 mL of dichloromethane over a period of 50 min. After the completion of addition, the mixture was stirred for an additional 20 h. The inorganic precipitate was removed by filtration, and the filtrate was washed with water, dried, and evaporated. The residue was subjected to a silica gel column chromatography. Elution with carbon tetrachloride gave a few yellow crystalline compounds in a small amount, structures of which could not be determined. The column was next eluted with dichloromethane, and eluates were evaporated and rechromatographed on a silica gel column. Elution with hexane/ethyl acetate (2:1) gave diazo ketone **23** (196 mg, 20%), mp 97 °C (lit.[25] mp 94 °C), and then dicyanonaphthalene **2** (16 mg, 1.6%), mp 233.5–234.5 °C (lit.[26] mp 232 °C).

Registry No. **2**, 5690-48-2; **3**, 191-48-0; *cis*-**12**, 83831-93-0; *trans*-**12**, 83831-94-1; **14**, 203-85-0; **15**, 29376-61-2; **16**, 51392-61-1; **17**, 83831-95-2; **18**, 208-96-8; **19**, 13019-33-5; **20**, 54736-49-1; **22**, 1932-07-6; **23**, 2008-77-7; 1*H*,3*H*-naphtho[1,8-*cd*]pyran, 203-84-9; 1,8-bis(hydroxymethyl)naphthalene, 2026-08-6; 1,2-dibromoacenaphthene, 14209-08-6.

(24) Berend, L.; Herms, J. *J. Prakt. Chem.* **1899**, *60*, 16.
(25) Cava, M. P.; Litle, R. L.; Napier, D. L. *J. Am. Chem. Soc.* **1958**, *80*, 2257–2267.
(26) Bradbrook, E. F.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1739–1744.

Oxidation of Sulfides by Acyclic α-Azohydroperoxides

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The oxidation of sulfides with a series of substituted benzylazobenzene α-hydroperoxides (**2a–f**) produced the corresponding sulfoxides in good yield (~90%) in C_6D_6 at 34 °C. The reaction was found to be of the first order with respect to α-azohydroperoxide and to sulfide in aprotic medium. The reaction of BzSPh with acyclic α-azohydroperoxide **2a** [MeOArCH(OOH)N=NPh] in C_6D_6 was found to be slower than the corresponding oxidation with 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole in $CDCl_3$. The relative reactivity series of sulfides with α-azohydroperoxide **2a** was found to be Me_2S (25) > BzSMe (14) > PhSMe (2.5) > BzSPh (1.0). This is similar to that observed for the reaction of the sulfides with hydrogen peroxide in protic solvent and reflects the relative nucleophilicities of the sulfides. The second-order rate constants for the reaction of a series of substituted benzylazobenzene α-hydroperoxides with PhSMe and BzSMe exhibited an excellent correlation with σ values. Both LFERs had ρ values of approximately 1.0. The results were interpreted to be consistent with nucleophilic attack of the sulfide on oxygen. Concomitant transfer of the hydroperoxy proton to the azo nitrogen would account for the lack of the requirement of general acid catalysis in aprotic medium.

The oxidation of sulfides to sulfoxides is readily accomplished[2] with peracids, hydrogen peroxide, and organic hydroperoxides. Sulfide oxidations are extremely rapid with peracids and show no dependence on acid catalysis. For hydroperoxides, S-oxidation reactions are generally characterized by the requirement of general acid catalysis. A general acid is apparently necessary in the transition state to facilitate the loss of ROH. In aprotic media, the hydroperoxide must serve as the general acid as well as the oxidant (the reaction rates become second order in hydroperoxide).

(1) Fellow of the Camille and Henry Dreyfus Foundation, 1981–1986.
(2) (a) Swern, D. "Organic Peroxides"; Wiley-Interscience: New York, 1971; Vol. II, pp 73–4. (b) Lewis, S. N. In "Oxidation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1969; Vol. I, Chapter 5, pp 244–6. (c) Barnard, D.; Bateman, L.; Cunneen, J. I. In "Organic Sulfur Compounds"; Kharasch, N. Ed.; Pergamon Press: London, 1961; Vol. I, Chapter 21, pp 229–46.

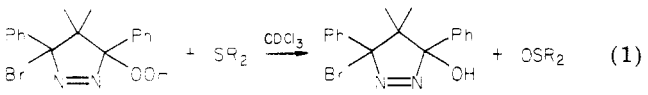
0022-3263/83/1948-0065$01.50/0

Table I. Yields of Sulfoxides and Secondary Decomposition Products of XArCH(OH)N=NPh for the Reaction of XArCH(OOH)N=NPh with Sulfides in C_6D_6 at 34 °C

X	[ROOH], M	sulfide	[sulfide], M	sulfoxide,[a,b] %	X-Ar-CHO,[a] %	XArC(O)NHNHPh[a] (isolated yield, %)
p-MeO	0.10	BzSPh	0.10	80	70	10
p-MeO	0.067		0.667	91	65	25
p-MeO	0.17	PhSMe	0.17	91	57	34
p-MeO	0.043		0.39	100		
p-MeO	0.34		0.085	100		
p-Me	0.17		0.17	91	15	75
p-H	0.34		0.34	76	11	65
p-F	0.17		0.17	100	24	75
p-Br	0.17		0.17	90	c.	90
m-NO_2	0.085		0.085	88	18	72
p-MeO	0.15	BzSMe	0.15	92	48	42 (23)
p-MeO	0.023		0.24	100		
p-Me	0.15		0.15	100	10	90 (70)
p-H	0.15		0.15	84	c.	84 (68)
p-F	0.15		0.15	93	c.	91 (70)
p-Br	0.15		0.15	85	c.	85 (66)
m-NO_2	0.15		0.15	100	20	80 (60)
p-MeO	0.077	Me_2S	0.077	100	17	80
p-MeO	0.20		0.77			(54)

[a] Determined by ^1H NMR integration relative to internal standard. [b] The yields of the primary product, XArCH(OH)N XArCH(OH)N=NPh were within experimental error of the yields of sulfoxide in all cases. [c] None observed.

Recently, we have shown[3] that 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole (1) will readily oxidize sulfides to sulfoxides in $CDCl_3$ without the requirement of general acid catalysis (reaction 1).



(1)

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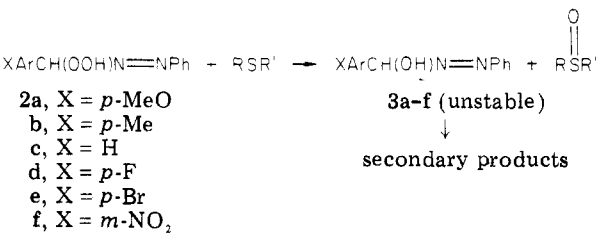
Bruice has shown[4] that the S-oxidation of thioxane by a flavin 4a-hydroperoxide (4a-FlEtOOH) does not require general-acid-catalyzed assistance for oxygen transfer. The reactions and relative reactivity of cyclic α-azohydroperoxide 1 closely parallel[3,5a] those of flavin 4a-hydroperoxides. Flavin 4a-hydroperoxides are involved in the oxygen atom transfer reactions of flavomonooxygenases. Many explanations[7] have been offered to explain the oxygen atom transfer chemistry of flavoenzyme monooxygenases. It is likely[6] that flavin hydroperoxides are the intermediates capable of oxygen atom transfer or at least the precursor to those intermediates in a number of biological systems.

The stereochemical and electronic factors that account for the enhanced reactivity ($\sim 10^5$) of 1[3,5] and FlEtOOH[4,6] as compared to those of alkyl hydroperoxides are not readily apparent. Hydroperoxide 1 is the only known example of a cyclic α-azohydroperoxide. There are few reports of systematic investigations of the electronic requirements on the reactivity of hydroperoxides in their reaction with sulfides. We report a study of the reaction of acyclic α-azohydroperoxides (benzylazobenzene α-hydroperoxides) with sulfides in benzene-d_6.

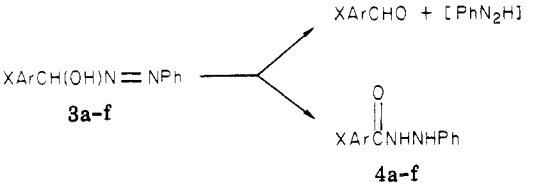
Results

A series of substituted benzylazobenzene α-hydroperoxides (**2a–f**, X-Ar-CH(OOH)-N=N-Ph) was prepared by the oxidation of the corresponding hydrazones with molecular oxygen.[8] The reaction of acyclic α-azohydroperoxides (**2a–f**) with a series of sulfides was carried out in C_6D_6 (Scheme I). In all cases, the sulfoxides were formed in good yield. The yields of the (metastable) benzylazobenzene α-hydroxides (**3a–f**) were found to be within experimental error of the yields of the corresponding sulfoxides. The alcohols **3a–f** were observable by NMR spectroscopy, but repeated efforts to isolate these compounds resulted only in the isolation of secondary decomposition products. **3a–f** were found to undergo decomposition (at variable rates) over the course of approximately 24 h under the reaction conditions to yield aldehydes and hydrazides (Scheme II).

Scheme I



Scheme II



The sulfoxides were isolated and proven to be identical with authentic samples by comparison of spectral properties. The secondary products (except PhN_2H) from the decomposition of **3a–f** were isolated and identified by comparison of spectral and physical properties with those of authentic samples and with reported values. Hydrazides were the major decomposition products for **3b–f** and were isolated in 60–70% yield from the BzSMe reaction mixture. Alcohol **3a** underwent decomposition to yield the

(3) Baumstark, A. L.; Chrisope, D. R. *Tetrahedron Lett.* **1981**, *22*, 4591.
(4) (a) Ball, S.; Bruice, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 6498. (b) Bell, S.; Bruice, T. C. *Ibid.* **1979**, *101*, 4017.
(5) (a) Baumstark, A. L.; Pilcher, R. S. *J. Org. Chem.* **1982**, *47*, 1141. (b) Baumstark, A. L.; Chrisope, D. R.; Landis, M. E. *Ibid.* **1981**, *46*, 1964.
(6) (a) Dugas, H.; Penney, C. "Bioorganic Chemistry"; Springer-Verlag: New York, 1981; pp 406–16. (b) Bruice, T. C. In "Biomimetic Chemistry"; Dolphin, D., Ed.; American Chemical Society: Washington DC, 1980; Chapter 6, pp 89–118.
(7) Reference 6 and references therein.
(8) Yao, H. C.; Resnick, P. *J. Org. Chem.* **1965**, *30*, 2832.

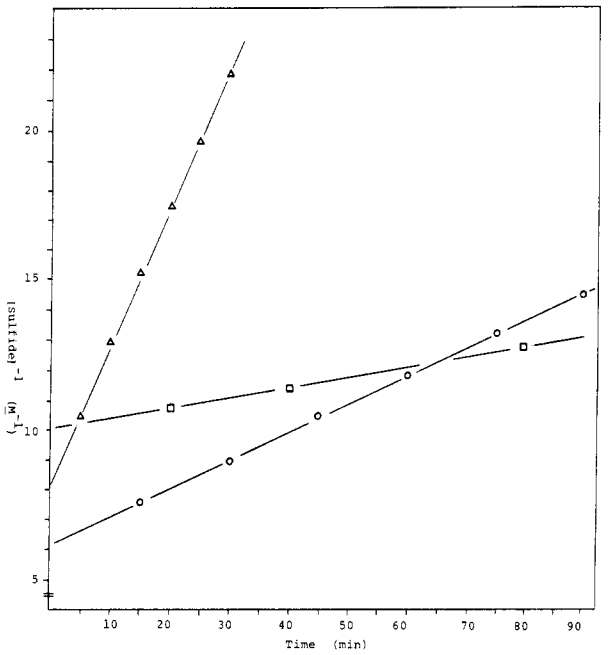


Figure 1. Second-order plots for the reactions of **2a** with equal molar quantities of sulfides: □, $[BzSPh]_0 = 0.10M$; ○, $[PhSMe]_0 = 0.17M$; △, $[BzSMe]_0 = 0.13$ M.

Table II. Second-Order Rate Constants for the Reaction of *p*-MeOArCH(OOH)N=NPh with RSR′ in C_6D_6 at 34 °C

sulfide	[ROOH], M	[sulfide], M	k_2, M^{-1} s^{-1}	rel reactivity
Me_2S	0.077	0.0774	1.3×10^{-2}	25
BzSMe	0.147	0.146	$7.3 \pm 0.3 \times 10^{-3}$	
	0.023	0.240	$7.0 \pm 0.2 \times 10^{-3}$	14
			av 7.2×10^{-3}	
PhSMe	0.34	0.085	1.3×10^{-3}	
	0.17	0.17	$1.4 \pm 0.2 \times 10^{-3}$	
	0.085	0.34	1.3×10^{-3}	
	0.041	0.328	1.3×10^{-3}	
			av 1.3×10^{-3}	2.5
BzSPh	0.10	0.10	$5.4 \pm 0.1 \times 10^{-4}$	
	0.066	0.667	4.7×10^{-4}	
		av 5.2	av 5.2×10^{-4}	1.0
PhSPh	0.15	0.60	too slow[a]	

[a] The rate of ROOH decomposition was faster than the rate of S-oxidation.

aldehyde as the major product in most cases. The product yields of sulfoxides and of secondary decomposition products of **3a–f** for the reaction of **2a–f** with a series of sulfides in C_6D_6 are listed in Table I.

α-Azohydroperoxide **2a** was the most stable[8] compound of the series **2a–f**; the kinetics of the reaction of a series of sulfides with **2a** was investigated in benzene-d_6 at 34 °C. The reaction was found to be of the first order with respect to both hydroperoxide and sulfide. Experiments with equal molar quantities of both reagents showed excellent second-order behavior (linear over at least 2 half-lives). Figure 1 shows the typical results obtained in these experiments. Reactions carried out under pseudo-first-order conditions (10-fold excess of sulfide) were linear over 2 half-lives and yielded second-order rate constants in excellent agreement with the other set of experimental conditions. Variation of the ratio of hydroperoxide to sulfide to 4:1 (from 1:1, 1:2, 1:4, or 1:10) also had no effect on the order of the reaction in hydroperoxide and again

Table III. Effect of the $[CO_3CO_2D]$ on the Second-Order Rate Constants for the Reaction of *p*-MeOArCH(OOH)N=NPh with BzSPh in C_6D_6 at 34 °C

[ROOH], M	[BzSPh], M	$[CD_3CO_2D]$, M	k_2, M^{-1} s^{-1}
0.10	0.20	0	5.4×10^{-4}
0.20	0.40	3.3×10^{-2}	1.2×10^{-3}
0.20	0.40	6.6×10^{-2}	2.9×10^{-3}
0.20	0.40	9.8×10^{-2}	4.5×10^{-3}

Table IV. Second-Order Rate Constants for the Reaction of Acyclic α-Azohydroperoxides 2a–f (XArCH(OOH)N=NPh) with Sulfides in C_6D_6 at 34 °C

x[a]	k_2[b] (BzSMe)	k_2[b] (PhSMe)
p-MeO	$7.2 \pm 0.2 \times 10^{-3}$	$1.3 \pm 0.2 \times 10^{-3}$
p-Me	$9.7 \pm 0.3 \times 10^{-3}$	$1.7 \pm 0.4 \times 10^{-3}$
p-H	$1.3 \pm 0.1 \times 10^{-2}$	$2.4 \pm 0.2 \times 10^{-3}$
p-F	$1.7 \pm 0.2 \times 10^{-2}$	$2.8 \pm 0.2 \times 10^{-3}$
p-Br	$2.3 \pm 0.2 \times 10^{-2}$	$4.2 \pm 0.3 \times 10^{-3}$
m-NO_2	$8.8 \pm 0.2 \times 10^{-2}$	$1.0 \pm 0.3 \times 10^{-2}$

[a] $[ROOH]_0 = [sulfide]_0 = 0.15$ M. [b] M^{-1} s^{-1}. Rate constants are the average of at least two experiments. Error represents standard average deviation. All rate constants determined by least-squares method; correlation coefficient ≥ 0.99 in all cases.

yielded values of k_2 in agreement with the previous values. Diphenyl sulfide was found to be essentially unreactive toward **2a** under reaction times that were limited due to the long-term instability of the α-azohydroperoxide. The kinetic data for the reactions of **2a** with PhSBz, PhSMe, BzSMe, and Me_2S are listed in Table II.

The results clearly showed that the reaction of acyclic α-azohydroperoxides was of the first order in hydroperoxide in aprotic medium. Clearly, general acid catalysis was not required for sulfide oxidation in these cases. Experiments were carried out in which CD_3CO_2D was added as a general acid in low concentrations. The α-azohydroperoxides were stable in the presence of low concentrations of CD_3CO_2D. The reaction of BzSMe with **2a** showed an increase in rate dependent upon the quantity of general acid added. The results are shown in Table III. The primary products of this catalyzed oxidation were identical with those in the normal oxidation. However, alcohol **3a** underwent rapid decomposition to the corresponding aldehyde with gas evolution.

The reactions of the series of α-azohydroperoxides **2a–f** with BzSMe and PhSMe were carried out in C_6D_6 at 34 °C. The reactions were found to be of the first order in hydroperoxide and of the first order in sulfide in all cases (as noted above). Under equal molar conditions, plots of inverse [sulfide] vs. time were linear for at least 2 half-lives for all cases. For the oxidations of both sulfides, the presence of electron-donating groups on the phenyl of the hydroperoxide slowed the reaction while the presence of electron-withdrawing groups increased the rate of S-oxidation. The values of k_2 (second-order rate constant) are listed in Table IV.

Hammett-type plots of the kinetic data of the reaction of **2a–f** with sulfides are shown in Figure 2. The data on the oxidation of the sulfides showed excellent LFERs vs. σ values. The ρ value ($\rho = 1.08 \pm 0.12$; $r = 0.997$) for the BzSMe oxidation is slightly greater than that ($\rho = 0.88 \pm 0.07$; $r = 0.998$) obtained for the PhSMe oxidation. The value of ρ for the PhSMe case may be low because the inherent instability of **2f**, (*m*-nitrobenzyl)azobenzene α-hydroperoxide, creates experimental difficulties for the measurement of the k_2 value. Pure **2f** is stable only for a limited time in solution. Partial decomposition of **2f** under the reaction conditions would result in low values

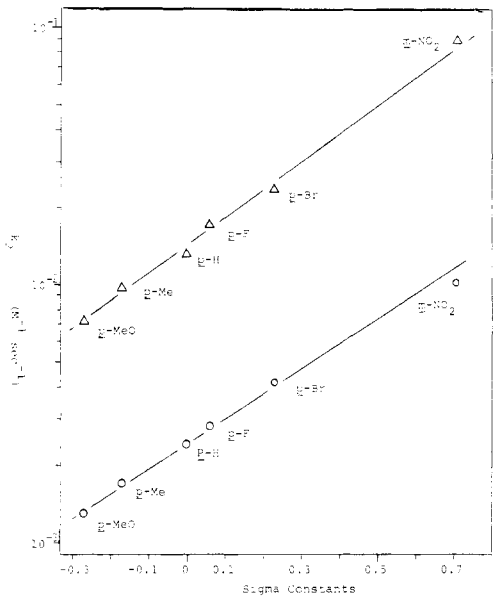


Figure 2. Hammett-type plots of the second-order rate constants (k_2) for the oxidation of PhSMe (○) and BzSMe (△) with **2a–f** in benzene-d_6 at 34 °C.

of k_2 for the less reactive sulfide.

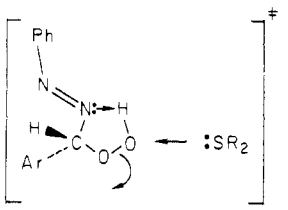
Discussion

α-Azohydroperoxides have been reported[9] to be a source of hydroxyl radical in anhydrous medium. Aromatic compounds were converted[9] to the corresponding phenols upon either photolysis or thermolysis of the α-azohydroperoxides. Recent results[3,5] with cyclic α-azohydroperoxide **1** suggested that the ionic oxygen atom transfer reactions of acyclic α-azohydroperoxides would be of interest. Acyclic α-azohydroperoxides were found to be approximately 10^2 times less reactive toward the oxidation of PhSMe in C_6D_6 than that of **1** with PhSMe in $CDCl_3$. Unfortunately, S-oxidations with acyclic α-azohydroperoxides **2a–f** could not be carried out in $CDCl_3$ due to the extreme instability of these compounds in that solvent.[8]

The acyclic α-azohydroperoxides were found to be less reactive toward S-oxidation than flavin hydroperoxides. The reaction of PhSMe with **2a** in C_6D_6 was approximately 1 order of magnitude slower than the corresponding S-oxidation by an isoalloxazine hydroperoxide (FlOOH)[10] in *tert*-butyl alcohol. The oxidation of thioxane in dry dioxane by another flavin peroxide, FlEtOOH, was found[4b] to be ~3 times faster than the oxidation of dimethyl sulfide by **2a**. However, the oxidation of thioxane in dry methanol by FlEtOOH was found[4,6] to be approximately 20 times faster than in dry dioxane. The flavin 4a-hydroperoxide containing intermediates in the bacteria luciferase reaction have been reported[11] to undergo an apparently rapid reaction with dialkyl sulfides. However, no product yields or rate constants were reported.

S-oxidations by H_2O_2 or alkyl hydroperoxides in aprotic medium are second order in hydroperoxide. A second molecule of hydroperoxide serves as a general acid in the transition state. Thus, the true non-acid-catalyzed process probably has not been observed in these cases. Judging from the results of Edwards,[12] oxidation of thioxane by hydrogen peroxide or *tert*-butyl hydroperoxide in dioxane is extremely slow. The reactivity of acyclic α-azohydroperoxides toward S-oxidation in aprotic medium appears to be at least 10^3 greater than that of hydrogen peroxide or alkyl hydroperoxides under similar conditions.

Scheme III



The relative reactivity series for the reaction of **2a** with sulfides [BzSPh (1.0) < PhSMe (2.5) < BsSMe (14) < Me_2 (25)] is similar to that calculated from the corresponding S-oxidations with hydrogen peroxide in protic medium with an acid catalyst[2e,13] [BzSPh (1.0) < PhSMe (1.8) < BzSMe (~8)]. This reactivity series corresponds to the nucleophilicity of the sulfides.

The ease of S-oxidation should correlate with the pK_a's of the alcohol products in the hydroperoxide reaction. The sign of the ρ values for the S-oxidation by α-azohydroperoxides is in agreement with this interpretation. The magnitude of the ρ values obtained for S-oxidation with α-azohydroperoxides in C_6D_6 is in agreement with that (ρ = 1.05) reported[14] for the oxidation of a dibenzyl sulfide with substituted perbenzoic acids in isopropanol. Since peracid S-oxidations have been shown not to require general acid catalysis and are actually slowed by protic solvents, the differences in the nature of the solvents for these two cases can probably be neglected. ρ values for the S-oxidation of substituted thioanisoles with hydrogen peroxide in aqueous ethanol (ρ = −1.17)[13] and that with FlOOH in *tert*-butyl alcohol (ρ = −1.67)[10] are of magnitude similar to those of this work and are in agreement with nucleophilic attack on oxygen by sulfur.

The lack of the requirement of general acid catalysis for S-oxidation has only been shown for flavin hydroperoxides, **1**, acyclic α-azohydroperoxides (**2a–f**), and peracids. The similar ρ values obtained for S-oxidation by peracids and α-azohydroperoxides suggest that both reactions have similar requirements. The mechanism of S-oxidation by peracids is well established and has been shown to involve intramolecular hydrogen bonding. Intramolecular hydrogen bonding would seem to be involved in the α-azohydroperoxide oxidations as well. By analogy with peracid and hydroperoxide S-oxidations, a mechanism involving nucleophilic attack of sulfur on the oxygen of the α-azohydroperoxide is consistent with the results. Concomitant transfer of the hydroperoxy proton to an azo nitrogen would explain the lack of the requirement for general acid catalysis (Scheme III).

Experimental Section

All solvents were of reagent grade. The sulfides were available commercially and were used without further purification. Melting points were recorded on a Thomas-Hoover (Uni-melt) capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian 360L spectrometer. IR spectra were recorded on a Perkin-Elmer 700 spectrometer. VPC studies were carried out on a Varian 920 preparative gas chromatograph by using a 6 ft × 0.25 in. SE-30 on chromosorb P column. Analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Preparation of α-Azohydroperoxides 2a–f. The α-azohydroperoxides were prepared by oxidation of the corresponding

(9) Tezuka, T.; Narita, N. *J. Am. Chem. Soc.* **1979**, *101*, 7413.
(10) Miller, A. *Tetrahedron Lett.* **1982**, *23*, 753.
(11) McCapra, F.; Hart, R. *J. Chem. Soc., Chem. Commun.* **1976**, 273.
(12) Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H. Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209.
(13) Modena, G.; Maiola, L. *Gazz. Chim. Ital.* **1975**, *87*, 1306.
(14) Overberger, C. G.; Cummins, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 4250.

Table V. Tabulation of Physical Data from the Preparation of α-Azohydroperoxides 2a-f

compd	mp, °C (lit. value)	isolated yield, % (lit. value)[a]	α-CH, δ[c]
2a	67-69 (67-68)[a]	65 (64)	6.33
2b	69-70 (69-70)[a]	66 (70)	6.30
2c	88-89 (88-89;[a] 83-84[b])	85 (85)	6.27
2d[d]	60-61	74	6.25
2e[f]	74-75	70	6.20
2f	88-89 (83-84)[a]	73	6.07

[a] See ref 15. [b] See ref 8. [c] 0.15 M solutions in C_6D_6 with 1% Me_4Si; $\rho = -0.27 \pm 0.03$, $r = 0.99$; see ref 16. [d] Anal. ($C_{13}H_{11}N_2O_2Br$) C, H. [f] Anal. ($C_{13}H_{11}N_2O_2F$) C, H.

phenylhydrazones with molecular oxygen by a method similar to published procedures.[8,15] For **2a-c**, 2.0 g of hydrazone in 20 mL of dry benzene was magnetically stirred in the dark for approximately 12 h, open to the atmosphere. The benzene solution was concentrated at low temperature under reduced pressure. The α-azohydroperoxides crystallized upon addition of Petroleum Ether. (**Caution**: Danger of explosion! Pure dry samples of **2d** and **2e** exploded while sitting on a sheet of filter paper in the dark. Apparently, vibrations from the table surface caused the detonation. Samples of dry **2e** could be set off by simply tapping the filter paper upon which the crystals were sitting in the dark!) The compounds were recrystallized from benzene/petroleum ether to yield pure (yellow) samples of the α-azohydroperoxides. The above method was modified as follows for the preparation of α-azohydroperoxide **2f**. The hydrazone was placed in a pressurized bottle under 50 psi of O_2 for 30 min. Samples of **2a-f** were stored as the solids (slightly "wet" with benzene to prevent explosions) in the *dark* at −60 °C. The data for **2a-f** are listed in Table V.

Kinetic Studies. The following general procedure was employed. A small sample of (crystalline) α-azohydroperoxide (containing a small quantity of C_6D_6 to reduce danger of explosion) was removed from low-temperature storage and placed on a plastic weighing pan *in the dark*. α-Azohydroperoxide (0.034 mmol, approximately 20 mg) was added, as the solid, to a *new* 5-mm NMR sample tube containing 500 μL of benzene-d_6 (Merck, 1% Me_4Si). Anisole (5.0 μL) was added as an internal standard. The NMR spectrum was recorded, and the signals were electronically integrated. The desired quantity of sulfide was added, via syringe, to the solution at 34 °C and mixed by inverting the tube. The signals were recorded and integrated vs. time. Product yields were determined relative to internal standard. The tube was allowed to sit at room temperature for 24 h after complete oxidation of the sulfide. A final spectrum was then taken (after complete decomposition of the alcohols **3a-f**) and electronically integrated.

Product Studies. The sulfoxides were isolated by column chromatography from samples that were the combination of several individual kinetic runs. They were proven identical with authentic samples prepared by oxidation with *m*-chloroperbenzoic acid by comparisons of spectra data. The sulfoxides were also checked by gas chromatographic techniques.

The α-azohydroxides **3a-f** were not isolable. They were readily observable by NMR spectroscopy and were found to be stable in solution for up to several hours. After 24 h, **3a-f** had undergone complete decomposition. One set of products, the substituted benzaldehydes, was isolated by column chromatography. The hydrazides crystallized after approximately 24 h from the individual kinetic run reaction mixtures. Petroleum ether was added to the benzene-d_6 solution to crystallize the remaining hydrazide. The crude hydrazides were collected and recrystallized from benzene/petroleum ether. The isolated product yields are listed in Table I. The melting point data and literature references for the hydrazides are shown in Table VI.

Table VI. Physical Data for Substituted Benzoyl Phenylhydrazides from the Decomposition of 3a-f (XArCH(OH)N=NPh)

hydrazide	mp, °C	lit. mp, °C	ref
4a (*p*-MeO)	177-178	179	*Beilstein 15*, 326
4b (*p*-Me)	166-167	167	*Beilstein 15*, 262
4c (*p*-H)	167-168	168	*Beilstein 15*, 255
4d (*p*-F)[a]	177-178	177-179	*Chem. Abstr.* **1970**, *72*, P54978e
4e (*p*-Br)	198-199	198-200	*Beilstein 15*, 256
4f (*m*-NO_2)	156-157	158-159	*Beilstein 15*, 257

[a] Anal. ($C_{13}H_{11}N_2OF$) C, H, N.

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Registry No. **2a**, 2829-34-7; **2b**, 2829-32-5; **2c**, 2829-31-4; **2d**, 83844-91-1; **2e**, 83844-92-2; **2f**, 83844-93-3; **4a**, 15089-03-9; **4b**, 39719-02-3; **4c**, 532-96-7; **4d**, 1496-02-2; **4e**, 25938-97-0; **4f**, 7497-14-5; BzSPh, 831-91-4; PhSMe, 100-68-5; BzSMe, 766-92-7; Me_2S, 75-18-3.

(15) (a) Busch, W.; Dietz, W. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 3277. (b) Pausacher, K. H. *J. Chem. Soc.* **1950**, 3478. (c) Criegee, R.; Lohaus, G. *Ber. Dtsch. Chem. Ges.* **1951**, *84*, 219.

(16) The magnitude of the ^1H NMR chemical shift correlation for α-CH (**2a-f**) with Hammett substituent constants is larger than that for similar benzyl-type protons. See: Tribble, M. T.; Traynham, J. C. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; pp 143-201 and references therein.