trans.[37] This situation is most likely for ethyl formate (cf. the trans conformer, Figure 4b) and, indeed, the largest $^5J_{HH}$ is observed for this compound. As substituents are added to the β carbon, the optimum conformation around the C_α–C_β bond becomes less likely, as it requires gauche interactions between the γ carbon(s) and the ester oxygen. This is as observed in Table VI. For isobutyl formate, where the optimum conformation requires two gauche interactions, $^5J_{HH}$ becomes particularly reduced. A similar effect is observed for *tert*-butyl formate, in which we have deduced a cis acyl–oxygen bond. Unfortunately, these speculations involve presumptions of perfectly staggered forms and are based on a theoretical model[37] derived for hydrocarbons.

Conclusion

It seems clear that measurement of vicinal carbon–proton couplings can be useful in the analysis of conformations. Furthermore, these couplings seems to be related to much more easily measured carbon chemical-shift changes.

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Benzoin Oximes in Sulfuric Acid. Cyclization and Fragmentation

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The kinetics of the reaction of benzoin, α-methylbenzoin, and α-phenylbenzoin oximes with sulfuric acid in acetic acid, resulting in concurrent cyclization to the corresponding 1-hydroxyindoles and fragmentation to benzonitrile and benzaldehyde, acetophenone, or benzophenone respectively, have been investigated at several temperatures in 60–100% sulfuric acid. Cyclization predominates at higher acidities. Mechanisms involving initial protonation on both oxime and carbinol followed by either direct fragmentation or dehydration and cyclization are proposed based on rate vs. acidity data, oxime basicity and the effects of perdeuteration and substitution of the benzoin oximes.

While benzoin oxime cyclizes to 1-hydroxy-2-phenylindole in concentrated sulfuric acid,[2] fragmentation to benzaldehyde and benzonitrile has been observed under other acidic conditions.[3] We have explored the concurrent cyclization and fragmentation reactions of benzoin oxime over a range of acidities produced from appropriate mixtures of sulfuric acid and acetic acid. As mechanistic interpretations frequently can be made from the relationship between reaction rate and solvent acidity,[4] we initially determined the H_0 values of anhydrous sulfuric acid in acetic acid for the concentration range used in this investigation (50–95%) at the temperatures used for the kinetic determinations. In addition to the detailed investigation of the reactions of benzoin oxime we obtained limited kinetic data for ring perdeuterated benzoin oxime, for α-methyl and α-phenyl benzoin oximes, and for benzoin oxime methylated on the α-hydroxyl position. All the oximes used in this investigation had the anti (or α) geometry.

The results of the H_0 determinations in the range 50–95% sulfuric acid are in Table I. The indicators used, with sulfuric acid concentration range and appropriate pK values at 30, 50, and 70°, obtained by interpolation from the data of Tickle, Briggs, and Wilson,[5] are as follows: 2,6-dinitroaniline, 50–60%, −5.35, −5.28, −5.21; 2-bromo-4,6-dinitroaniline, 55–70%, −6.43, −6.26, −6.10; 2,4,6-trinitro-*m*-toluidine, 70–85%, −8.03, −7.80, −7.68; picramide, 85–95%, −9.82, −9.62, −9.42. Figure 1 shows the relationship H_0 vs. % H_2SO_4 w/w for solutions in water,[6] acetic acid,[7]

Table I
$-H_0$ Values Derived from Log I Ratios

H_2SO_4, % w/w	30° Log I	30° $-H_0$	50° Log I	50° $-H_0$	70° Log I	70° $-H_0$
	2,6-Dinitroaniline (606-22-4)					
	(pK = −5.35)		(pK = −5.28)		(pK = −5.21)	
50	+0.66	6.01	+0.47	5.75	+0.29	5.50
55	+1.10	6.45	+0.97	6.25	+0.81	6.62
60	+1.51	6.86	+1.35	6.63	+1.26	6.47
	2-Bromo-4,6-dinitroaniline (1817-73-8)					
	(pK = −6.43)		(pK = −6.26)		(pK = −6.10)	
55	+0.05	6.48	−0.10	6.36	−0.08	6.02
60	+0.50	6.93	+0.37	6.63	+0.40	6.50
65	+0.85	7.28	+0.75	7.01	+0.65	6.75
70	+1.28	7.71	+1.14	7.40	+1.05	7.15
	2,4,6-Trinitro-*m*-toluidine (22603-58-3)					
	(pK = −8.03)		(pK = 7.80)		(pK = −7.68)	
70	−0.37	7.66	−0.47	7.33	−0.58	7.10
75	+0.17	8.20	+0.10	7.90	−0.14	7.54
80	+0.59	8.62	+0.47	8.27	+0.36	8.04
85	+1.01	9.04	+0.99	8.79	+0.86	8.54
	Picramide (489-98-5)					
	(pK = −9.82)		(pK = −9.62)		(pK = −9.42)	
85	−0.69	9.13	−0.79	8.83	−0.92	8.50
90	−0.29	9.53	−0.41	9.21	−0.64	8.78
95	+0.27	10.19	+0.30	9.92	+0.19	9.61

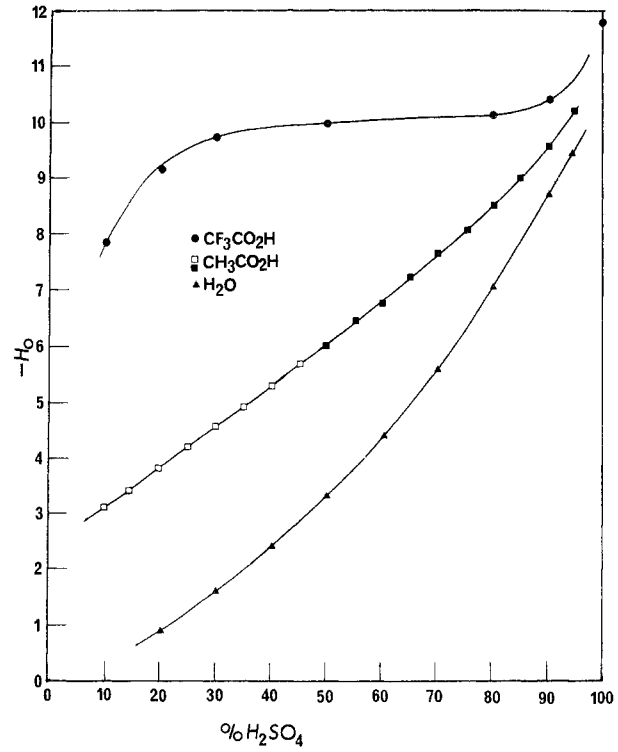


Figure 1. Acidity function, $-H_0$ vs. % H_2SO_4; ■, present work, □, ref 7; ▲, ref 6; ●, ref 8.

Table II
Kinetic Parameters for the Cyclization and Fragmentation of α-Benzoin Oxime

$-H_0$	30° k_c, sec^{-1}	30° k_f, sec^{-1}	50° k_c, sec^{-1}	50° k_f, sec^{-1}	70° k_c, sec^{-1}	70° k_f, sec^{-1}	% H_2SO_4
6.86	1.38×10^{-6}	1.77×10^{-6}					
6.63			4.36×10^{-6}	7.23×10^{-6}			60
6.45					2.25×10^{-5}	3.56×10^{-5}	
8.20	6.3×10^{-5}	2.82×10^{-5}					
7.90			1.76×10^{-4}	1.26×10^{-4}			75
7.54					4.67×10^{-4}	3.53×10^{-4}	
9.13	8.90×10^{-4}	2.81×10^{-4}					
8.83			2.81×10^{-3}	1.40×10^{-3}			85
8.50					7.16×10^{-3}	5.59×10^{-3}	
10.19	3.54×10^{-2}	3.53×10^{-3}					
9.92			1.10×10^{-1}	1.75×10^{-2}			95
9.62					2.96×10^{-1}	7.96×10^{-2}	
11.84	14.2	3.16×10^{-1}					100

and trifluoroacetic acid.[8] A check on our data stems from the observation that our curve smoothly intercepts that of Hall and Spengeman,[7] which terminates at approximately 50% sulfuric acid. The 100% sulfuric acid value is that determined by Vinnik.[9]

The rates of the cyclization and fragmentation reactions were determined at 30, 50, and 70°. The appearance of 1-hydroxy-2-phenylindole was cleanly first order to at least 4 half-lives. Infinity values were obtained at about 6 half-lives and where reproducible when the apparatus was swept with dry nitrogen throughout the reaction. In most cases a computer-generated infinity value was also determined, by finding the value of $A_{\infty e}$ which gave the best linear presentation of the first-order relationship log $A_{\infty e}/(A_{\infty e} - A_t)$ vs. t. In most instances the calculated and experimental value were in close accord. The values of rate constants for the fragmentation reactions were determined indirectly considering the cyclization and fragmentation to be two parallel first-order reactions with a common starting material.

The rates of cyclization and fragmentation (Table II) were obtained at 30, 50, and 70° over a wide range of acidities (55–95% sulfuric acid). The Hammett–Zucker plots of log k_c and log k_f against H_0 over this range of acidities and at all reaction temperatures were slightly curved with the slope increasing at higher acidities (Figures 2 and 3). The slopes at the different temperatures were almost parallel.

These curves gave slopes of about 1.3 for the plot of log k_c against $-H_0$ and about 1.0 for the plot of log k_f against $-H_0$, both at 30°. At other temperatures the results are very similar.

In addition to the extensive data obtained for benzoin oxime, a series of substituted benzoin oximes was investigated at $H_0 = -10.2$ and at 30°. Replacing the α hydrogen of the benzoin oxime by deuterium, methyl, or phenyl groups gave compounds which reacted analogously to benzoin oxime but at differing rates. In all cases the corresponding hydroxyindole was formed as well as the fragmentation products: benzonitrile, and benzaldehyde, acetophenone, or benzophenone, respectively. The rates of the fragmentations and cyclizations differed from that of benzoin oxime and are shown in Table III. Additionally benzoin methyl ether oxime was investigated. This compound gave mainly cyclization; much less fragmentation was ob-

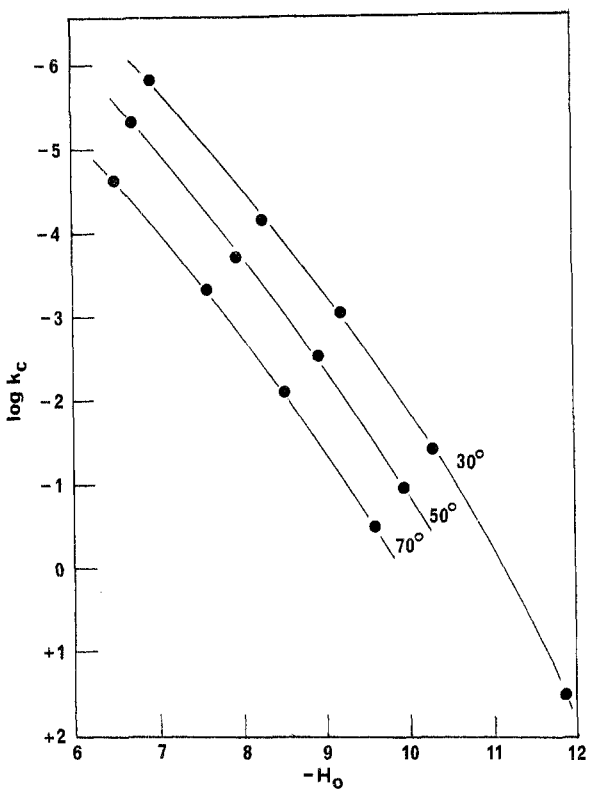


Figure 2. Hammett–Zucker plot for cyclization reactions.

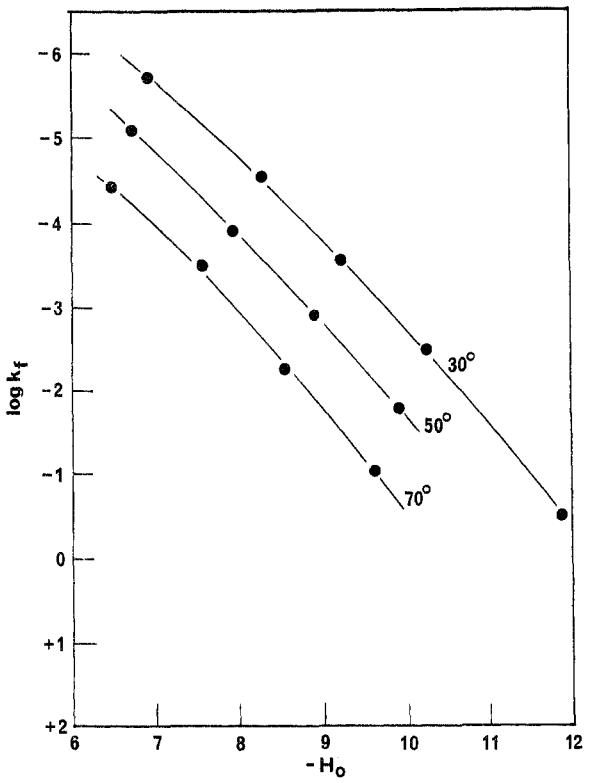


Figure 3. Hammett–Zucker plot for fragmentation reactions.

Table III
Effect of Substitution on Cyclization and Fragmentation at $H_0 = -10.2$ at 30°

Substitution (etc.)	k_c, sec^{-1}	k_f, sec^{-1}	Registry no.
α-H	3.54×10^{-2}	3.53×10^{-3}	441-38-3
α-Me	8.87×10^{-2}	5.89×10^{-3}	889-89-4
α-Ph	7.34×10^{-2}	1.47×10^{-2}	56830-59-2
α-OCH_3	3.27×10^{-2}	6.87×10^{-4}	56830-60-5
Perdeuterio	3.66×10^{-2}	3.68×10^{-3}	56830-61-6

Table IV
Kinetic Parameters in Trifluoroacetic Acid at 30°

H_2SO_4, M	$-H_0$	k_c, sec^{-1}	k_f, sec^{-1}
4.3	9.0	1.44×10^{-5}	6.30×10^{-5}
11.5	9.4	1.12×10^{-4}	1.58×10^{-4}
17.7	10.2	8.32×10^{-3}	3.37×10^{-3}

served. Finally we briefly examined the effect on reaction rate of substituting trifluoroacetic acid for acetic acid (Table IV). These reaction mixtures were prepared by interpolation from the data of Hyman and Garber.[8] The values obtained for k_c were considerably less in trifluoroacetic acid than in acetic acid at the same H_0. The k_f values were much less sensitive to solvent change. Substitution of acetic acid for water results in a significant increase in solution acidity at similar concentrations of sulfuric acid. Hall and Spengeman[7] observed a 3 H_0 unit separation between the parallel curves for acetic acid and water solutions to about 50% sulfuric acid. We have found that beyond this point the curves converge and extrapolate smoothly to the value for anhydrous sulfuric acid ($H_0 = -11.94$). Because of the limited number of points delineating the acidity function curve, the present data, while adequate for this study, do not claim the precision and accuracy of more definitive investigations. In particular we omitted the interesting range 95–100% sulfuric acid because we desired kinetic data over a wide range of sulfuric acid concentrations. Because of the high sulfuric acid concentrations used, the problem of ion-pair formation resulting from the low dielectric constant of acetic acid[10] can be minimized and the system should behave similarly to aqueous systems. Assuming an approximately linear variation of dielectric constant with mole fraction we can estimate that the minimal value of dielectric constant for the solutions will be about 46.

A number of factors are germane to the mechanism of fragmentation and cyclization of benzoin oxime in strong acid. Oximes are quite basic; for example, cyclohexanone oxime is claimed to be completely monoprotonated in 2.5×10^{-2} M sulfuric acid[11] and potentiometric titrations have shown values near zero for the pK_a's of several oximes.[12] Consequently, benzoin oximes are monoprotonated, even at the lowest acidities used in this investigation. In benzoin oximes sites for protonation are limited. Initial protonation will occur at the oxime on either oxygen or nitrogen, with the former site preferred from a comparison of the pK_a's of alcohols, imines, and oximes.[12] A second protonation can occur on the carbinol oxygen (alcohols have pK_a's in the range −2 to −5[12]) or much less easily again on the oxime or its adjacent carbon. If diprotonated structures are involved in the fragmentation or cyclization reactions, the former possibility is more plausible and indeed one would expect that appreciable carbinol protonation would occur at the higher acidities used in this investigation.

In a detailed study of the Beckmann rearrangement in strong acid,[11] Vinnik and Zarakhani have convincingly demonstrated that dehydration of the conjugate acid of the oxime to an iminium ion or ion pair intervenes and that this process only becomes important at reasonably high acidities, e.g., $-H_0 > 8$. If this is the case in the present study fragmentation and/or cyclization may also require this step. Fragmentation is the major reaction at the lower acidities while crossover to cyclization occurs near $H_0 = -7$ and this becomes the predominant reaction at the highest acidities. In the absence of solvent effects fragmentation and cyclization reactions must arise from two different in-

Table V
Activation Parameters for Benzoin Oxime Cyclization obtained at H_o = −9.5 by Interpolation of Rate Data

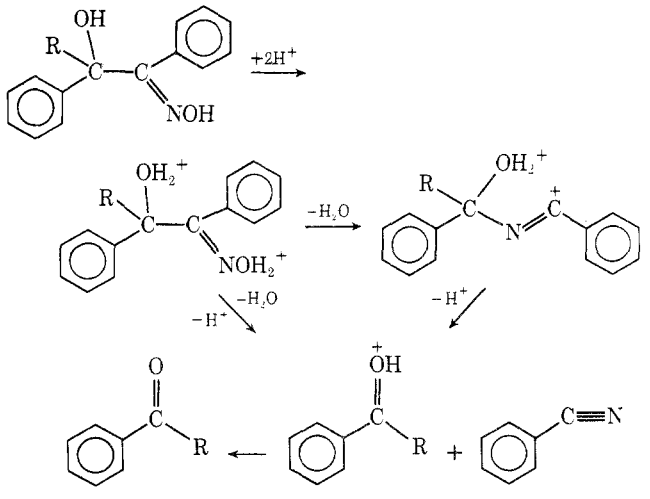
	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol deg
Cyclization	21.1	−2.8
Fragmentation	25.5	+9.9

termediates, because, although the Zucker–Hammett plots of log k_f and log k_c vs. $-H_0$ are reasonably linear curves over the range of H_0 values studied, the slopes are different (1.0 and 1.3, respectively) and the ratio of k_f to k_c is acidity dependent.

The use of Zucker–Hammett criteria as a mechanistic probe in the current investigation, rather than the more recent Bunnett parameters[13] w, w^*, ϕ is justified because these latter criteria are only strictly applicable to aqueous systems where the large body of experimental evidence allows valid mechanistic correlations to be made. This is not the case for nonaqueous systems, particularly sulfuric acid–acetic acid solutions where experimental results are very limited. The reasonable linearity and the slopes of the Zucker–Hammett plots for both fragmentation and cyclization suggests that proposed mechanisms for these reactions should be consistent with A-1 processes where equilibrium protonations precede an unimolecular rate-determining step which does not involve solvent.

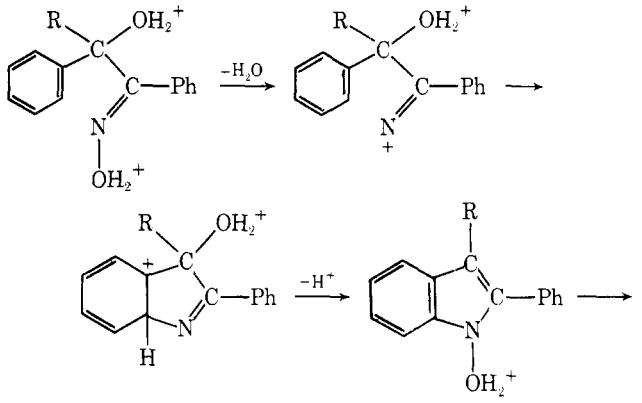
The above observations afford convenient rationalizations for the observed crossover in rates and their acidity dependence and allow several reasonable mechanistic possibilities to be proposed.

Because fragmentation predominates at lower acidities the following schemes, both involving protonation on the carbinol but occurring without intermediacy of iminium ions, are suggested: direct fragmentation or, by analogy with Grob's proposals for fragmentation of α-aminoketoximes,[14] via an intermediate nitrilium ion.

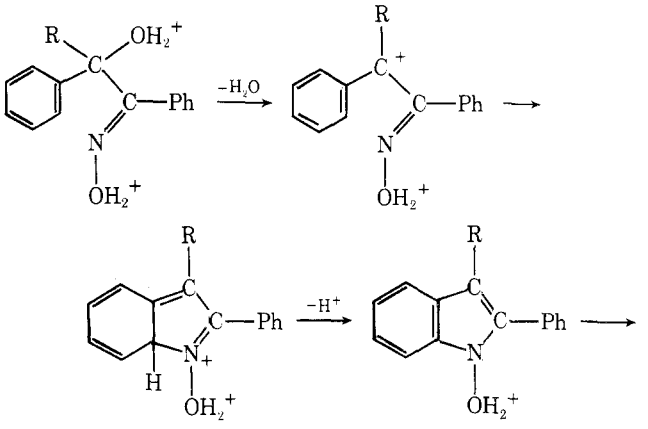


In any case the rate-determining step is probably the fission of the C–C or C–N bond to give the carbonyl compound and the nitrile. Subsequent hydrolysis of the nitrile to the amide and air oxidation of the carbonyl to the carboxylic acid may accompany this phase of the reaction or subsequent work-up as shown by the mass balance experiments.

The generation of the electrophilic iminium ion affords a species which can also easily lead to ring closure. The predominance of cyclization at the higher acidities suggests that acidity plays a further role in the cyclization and it is reasonable to suppose that this involves formation of the iminium ion. Cyclization shows only a small secondary deuterium isotope effect consistent with proton loss and aromatization not being the rate-determining step. Further, the rate of cyclization is not particularly sensitive to conjugative effects of substituents at the carbinol carbon and thus the formation of a carbonium ion at this site is also not involved in a rate-determining step. A tentative scheme can be constructed for the cyclization as follows.



Quenching of completed reactions in sulfuric acid with methanol or acetic acid fails to yield N-methoxy or N-acetoxy products which suggests that rapid transfer of water from position 3 to the nitrogen occurs and that an indolium ion does not intervene in the reaction. The timing of the dehydration of the oxime and the carbinol could conceivably be reversed so that rate-determining attack of the oxime nitrogen lone pair on the aromatic ring, activated by the adjacent carbonium ion, could occur; this sequence of steps maintains the integrity of the oxime oxygen in the final product.



Limited data obtained in trifluoroacetic acid instead of acetic acid suggest that the concentration of sulfuric acid as well as solution acidity is important. The lower rates of cyclization in the former solvent may be interpreted as a medium effect where the decreased dielectric constant resulting from the lower sulfuric acid concentrations retards the formation of the iminium or carbonium ions. Interestingly, however, at H_0 = −10.2, where the assumption that dielectric constant is proportional to mole fraction results in approximately equal values of dielectric constant for these solvent systems, the rate of cyclization is about fourfold slower.

The activation parameters for the reactions (Table V), which, because of the variation of H_0 with temperature, were obtained by interpolation at H_0 = −9.5, were unexceptional. The values of $\Delta H^{\ddagger}$ for cyclization and fragmentation lie between 20 and 25 kcal/mol and are very typical of

enthalpies of activation observed for a wide variety of oxime rearrangements and fragmentations in a variety of solvents.[11,15] Too much stress cannot be placed on the values of $\Delta S^{\ddagger}$ obtained, although the values of −2.8 and +9.8 cal/mol deg for cyclization and fragmentation, respectively, are reasonable for such processes. The complex nature of the equilibria intervening before and after the proposed rate-determining steps in each case reduce the significance of the entropy of activation in the absence of data for these intervening steps.

Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. NMR spectra were obtained on a Varian T-60 spectrometer in $CDCl_3$.

Sulfuric acid (100%) was obtained from reagent grade material and sufficient oleum. It had mp 10.3°.[16] Anhydrous acetic acid was obtained by distilling reagent grade acetic acid from phosphorus pentoxide, followed by fractional distillation. It had mp 16.5°.[17] The Hammett indicators were purified by column chromatography on neutral alumina followed by recrystallization from aqueous ethanol. 2,4,6-Trinitro-*m*-toluidine was prepared as described;[18] the others were commercial samples. After purification all had melting points and spectra which agreed with reported values.

Benzoin oxime,[19] α-methylbenzoin oxime,[20] α-phenylbenzoin oxime,[21] and benzoin methyl ether oxime[2] were prepared by published procedures.

Samples of the hydroxyindoles were prepared by dissolving the appropriate oximes in concentrated sulfuric acid and stirring the solution, under nitrogen, for about 12 hr at room temperature. Dilution with ice, filtration, and two recrystallizations from ethanol afforded the pure compounds.

1-Hydroxy-2-phenylindole: mp 168° (lit.[2] mp 175°); uv max (65% aqueous acetic acid containing 0.5 *M* sodium acetate) 302 nm (ε 17050).

1-Hydroxy-2-phenyl-3-methylindole: mp 158–160°; uv max (same solvent) 310 nm (ε 18340).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.54; H, 6.01; N, 6.48.

1-Hydroxy-2,3-diphenylindole: mp 195–197° dec; uv max (same solvent) 321 nm (ε 16960).

Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 83.97; H, 5.56; N, 4.93.

1,1′,2,2′,3,3′,4,4′,5,5′-Decadeuteriobenzoin. A slow stream of chlorine gas was passed into refluxing toluene-d_8 (10 g, 0.1 mol) with irradiation by a sun lamp until there was a weight increase of 7.4 g. The mixture was distilled at 96–100° (22 mm) and the distillate was refluxed under nitrogen with a mixture of calcium carbonate (8 g) and water (30 ml) for 4 hr. Additional water (150 ml) was added and the mixture distilled until the distillate was clear. The distillate was adjusted to pH 8 with sodium carbonate and extracted with methylene chloride (3 × 25 ml). The extract was dried ($MgSO_4$) and evaporated. The residue of benzaldehyde-d_6, without purification, was dissolved in ethanol (10 ml) and potassium cyanide (0.1 g) in water (1 ml) was added. The mixture was refluxed under nitrogen for 2 hr, cooled, and diluted with an equal volume of water. The slightly oily precipitate was filtered and crystallized from aqueous ethanol. Perdeuteriobenzoin was isolated as almost colorless crystals, mp 135–138°, 5.7 g (52% based on toluene-d_8).

The NMR spectra showed a doublet at δ 5.95 (~0.1 H relative to the –OH signal at δ 4.58) and a series of weak peaks at δ 7.4 and 7.9 due to aromatic protons. Integration relative to the OH signal showed that the rings were <1% protonated.

After three recrystallizations from aqueous methanol containing a few drops of 2 *N* NaOH the NMR peak at δ 5.95 gave 1 H.

The oxime was prepared in the usual way.

Acidity Functions. These were determined essentially as described by Tickle, Briggs, and Wilson,[5] and by Jorgenson and Hartter.[18] Aliquots of indicator stock solutions (in acetone or methylene chloride) were pipetted into volumetric flasks, the solvent was removed in vacuo, and the indicator was dissolved in appropriate sulfuric acid–acetic acid mixtures at 30, 50, or 70°. Spectra, with the same acid mixture as reference, were determined on a Beckman DB-GT spectrophotometer with a Beckman 10-in. recorder. Temperature control was obtained with a Haake Model E52 thermocirculator. Solutions were equilibrated in the spectrometer for about 10 min before spectra were determined.

The molar absorptivities, ϵ_{In} and ϵ_{HIn^+}, were obtained at appropriate wavelengths about 2 H_0 units below the pK_{In} of the indicator and in 100% sulfuric acid, respectively. Log I was determined as $\log (\epsilon_{In} - \epsilon_{obsd})/(\epsilon_{obsd} - \epsilon_{HIn^+})$ and thus

$$H_0 = pK_{HIn^+} - \log I$$

Rate Data. These were obtained as follows. The oxime was dissolved in a small amount of anhydrous acetic acid in one bulb of a two-bulb apparatus. Sulfuric acid–acetic acid mixture of such a concentration that addition of the acetic acid from the first bulb would give the required H_0 value was placed in the second bulb. The apparatus was purged continuously with dry nitrogen. After thermal equilibrium was established the solutions were mixed, aliquots were withdrawn with a calibrated pipet at noted time intervals and quenched in 65% aqueous acetic acid containing 0.5 *M* sodium acetate, and the spectra were determined immediately. 1-Hydroxy-2-phenylindole was determined spectrophotometrically at 302 nm; the 1-hydroxy-2-phenyl-3-methyl- and 1-hydroxy-2,3-diphenylindoles were determined at 310 and 321 nm, respectively.

The rate constants k_c and k_f were obtained by considering the cyclization and fragmentation to be the only reactions occurring to a significant extent[22] and as parallel first-order processes. A least-squares plot of $\log A_{\infty e}/(A_{\infty e} - A_t)$ vs. time yields $(k_c + k_f)$. If $A_{\infty c}$ is the calculated infinity absorbance, assuming only cyclization, obtained for pure 1-hydroxy-2-phenylindole, and $A_{\infty e}$ is the experimental infinity absorbance, then

$$k_c/k_f = A_e/(A_{\infty c} - A_{\infty e})$$

and k_c and k_f can be evaluated independently.

Because of the difficulty in some experiments in obtaining consistent values of $A_{\infty e}$, a simple incremental computer procedure was used such that a value of $A_{\infty e}$ was determined so that $\log [A_{\infty e}/(A_{\infty e} - A_t)]/t$ was constant at all experimentally determined values of A_t. The values of $A_{\infty e}$ thus obtained were usually close to and often identical with those measured at about 6 half-lives.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined at $-H_0 = 9.5$ from values of log k_c and log k_f obtained by interpolation on the Hammett–Zucker plots.

Product Analyses and Mass Balance. In a typical experiment benzoin oxime (11.35 g, 0.05 mol) was dissolved, under nitrogen, in a mixture of anhydrous sulfuric acid (65 g) and anhydrous acetic acid (35 g) ($H_0 \simeq -7.2$). After about 6 hr on a steam bath and about 12 hr at room temperature the yellow solution was poured onto ice (500 g) and the mixture immediately extracted with methylene chloride (5 × 75 ml). The extract was washed thoroughly with 5% sodium bicarbonate to remove the benzoic and acetic acids and then shaken under nitrogen with 2 *N* sodium hydroxide (3 × 50 ml) to extract the hydroxyindole. The cooled sodium bicarbonate extract was acidified and extracted with methylene chloride which was washed with water and evaporated to yield benzoic acid (1.52 g, 0.0125 mol). The cooled sodium hydroxide extract was cautiously acidified with concentrated hydrochloric acid and filtered to yield crude 1-hydroxy-2-phenylindole (5.08, 48.4%, 0.024 mol) as yellow crystals, mp 164–168°. One recrystallization from ligroin–chloroform raised the melting point to 170–171° (lit.[2] 175°). The original methylene chloride solution was evaporated and the pale yellow oily residue was chromatographed on silica gel (500 g). Elution with petroleum naphtha (bp 60–80°) and increasing amounts of methylene chloride eluted in sequence benzaldehyde (1.03 g, 0.01 mol), benzonitrile (0.85 g, 0.008 mol), and benzamide (1.68 g, 0.014 mol). Assuming hydrolysis and air oxidation, this accounted for 0.0448 mol of starting material. Thus the mass balance was 94%.[22] Data obtained at other H_0 values were always near 95%. Similar data were obtained for α-methyl and α-phenyl benzoin oxime.

Registry No.—1-Hydroxy-2-phenylindole, 1859-39-8; 1-hydroxy-2-phenyl-3-methylindole, 56830-62-7; 1-hydroxy-2,3-diphenylindole, 56830-63-8; perdeuteriobenzoin, 56830-64-9.

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On Fragmentation of Aryl Sulfide Radical Anions during Aromatic SRN1 Reactions[1]

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The photostimulated reaction of ethanethiolate ion with iodobenzene in liquid ammonia produces not only ethyl phenyl sulfide but also thiophenoxide ion and diphenyl sulfide. This shows that the presumed intermediate in the SRN1 mechanism, the ethyl phenyl sulfide radical anion, fragments in part into ethyl radical and thiophenoxide ion. The reactions of *p*-iodoanisole with thiophenoxide ion and of iodobenzene with *p*-methoxythiophenoxide ion both produce phenyl *p*-methoxyphenyl sulfide in good yield without any detectable amount of symmetrical diaryl sulfide, indicating that the phenyl *p*-methoxyphenyl sulfide radical anion intermediate does not fragment appreciably in this system. Reactions of four unsymmetrical phenyl aryl sulfides with acetone enolate ion afford more *m*-methyl-, *p*-methyl-, *m*-methoxy-, or *p*-methoxyphenylacetone than phenylacetone.

Diaryl sulfides and alkyl aryl sulfides are cleaved cathodically or by alkali metals to form an arenethiolate ion and a hydrocarbon (eq 1), the necessary hydrogen atom being derived from the solvent.[2-7]

$$\mathrm{ArSR} \xrightarrow{2e} \mathrm{ArS^-} + \mathrm{RH} \qquad (1)$$

Both stoichiometry[6] and polarographic data[7] indicate a two-electron process. However, there is evidence that an alkyl[6] or aryl[8] radical is formed as a primary cleavage fragment, as well as the arenethiolate ion. It follows that the aryl sulfide radical anion is the entity which actually fragments (eq 2).

$$[\mathrm{ArSR}]\cdot^- \longrightarrow \mathrm{ArS^-} + \mathrm{R}\cdot \qquad (2)$$

In aromatic substitution by the SRN1 mechanism,[9] the radical anions of aryl sulfides sometimes appear as intermediates.[10-14] In Scheme I, this radical chain mechanism is

Scheme I

$$\mathrm{ArX} + \text{electron source} \longrightarrow [\mathrm{ArX}]\cdot^- + \text{residue} \qquad (3)$$

$$[\mathrm{ArX}]\cdot^- \longrightarrow \mathrm{Ar}\cdot + \mathrm{X^-} \qquad (4)$$

$$\mathrm{Ar}\cdot + \mathrm{Y^-} \longrightarrow [\mathrm{ArY}]\cdot^- \qquad (5)$$

$$[\mathrm{ArY}]\cdot^- + \mathrm{ArX} \longrightarrow \mathrm{ArY} + [\mathrm{ArX}]\cdot^- \qquad (6)$$

$$\text{termination steps} \qquad (7)$$

presented in generalized form.[15] When a diaryl sulfide is involved as substrate (ArX), the fragmentation of its radical anion, $[\mathrm{ArX}]\cdot^-$, occurs in step 4. When a thiolate ion is involved as nucleophile ($\mathrm{Y^-}$), the species $[\mathrm{ArY}]\cdot^-$ formed in step 5 is an aryl sulfide radical anion, and conceivably it might suffer fragmentation before transferring an electron to another substrate molecule in step 6.

In the present investigation, we address a number of questions suggested by this discussion. If an alkanethiolate ion is employed as nucleophile $\mathrm{Y^-}$, will radical anion $[\mathrm{ArY}]\cdot^-$ fragment before it loses its "extra" electron? If an arenethiolate nucleophile, $\mathrm{Ar'S^-}$, is employed, with an aryl group different from that in substrate ArX, will the radical anion $[\mathrm{ArSAr'}]\cdot^-$ formed in step 5 fragment to Ar'· and $\mathrm{ArS^-}$, leading eventually to products $\mathrm{Ar_2S}$ and/or $\mathrm{Ar'_2S}$ as well as ArSAr'? If an unsymmetrical diaryl sulfide, ArSAr', is used as substrate in photostimulated reaction with acetone enolate ion,[11] in what proportions will the two arylacetones $\mathrm{ArCH_2COCH_3}$ and $\mathrm{Ar'CH_2COCH_3}$ be formed? Inasmuch as each of these questions has required separate investigation, we shall present and discuss the results from each before moving on to the next.

I. Reaction of Iodobenzene with Ethanethiolate Ions. Although the photostimulated reaction of iodobenzene with excess thiophenoxide ion in ammonia is quite fast, giving a nearly quantitative yield of diphenyl sulfide in 70 min,[12] that of iodobenzene with ethanethiolate ion is much slower. Under similar conditions, only 60% of iodide ion was released in 90 min. The products from an extended (200 min) reaction included 30% of ethyl phenyl sulfide and 3% of diphenyl sulfide.

Formation of the latter product suggested the intermediacy of thiophenoxide ion. A further run was performed under the same conditions, the ammonia was allowed to evaporate, and ethyl iodide was added to convert any thiophenoxide ion to ethyl phenyl sulfide. The yield of the latter was thereby raised to 61%, supporting the hypothesis. In a further experiment of similar type, benzyl chloride was added to benzylate the thiophenoxide ion, and 44% of benzyl phenyl sulfide was formed.

The reaction of iodobenzene with ethanethiolate ion, in ammonia under irradiation, thus gives products as indicated in eq 8.

$$\mathrm{PhI} + \mathrm{EtS^-} \xrightarrow[\mathrm{NH_3}]{h\nu} \underset{30\%}{\mathrm{PhSEt}} + \underset{44\%}{\mathrm{PhS^-}} + \underset{3\%}{\mathrm{Ph_2S}} \qquad (8)$$