

- of 0.000 417 amu. Dr. Vincent Williams (see Acknowledgment) has pointed out to us a rationale for the difference in the mass spectra of **3** and **4** (unusual for isomers). He suggests that the base peak at 148 is due to a retro-Diels-Alder decomposition for **4** as shown.
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 (36) It was suggested from the chemical shift data that the hydrogen bond in **1** was actually stronger than in **A**.
 (37) Coupling constants should be independent of the solvent assuming no conformational change in the substrate. We feel that the conformations should be almost identical in either Me_2SO-d_6 or acetone- d_6 due to the similarity in polarity and hydrogen-bonding ability.
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 (48) We feel that the chemical behavior of the tetrahydro epoxide (i.e., **5**) and dihydrodiol epoxides (i.e., **A** and **B**) toward nucleophilic attack by phosphate should be identical. Attack should occur at the benzylic carbon of the oxirane ring and yield a monoalkyl phosphate derivative which is α to a trans hydroxyl group. The presence of the trans hydroxyls as opposed to the two protons at the remaining two carbons of the saturated ring should have little effect on the stability of a phosphate adduct.
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 (54) For indene oxide in $NaClO_4$ the ratio of trans:cis diol was 37:2 while in KCl the ratio was 29:3. We do not know if the change from 37 to 29 is within experimental error. The increase in cis diol from 0 to 15% in this study is outside experimental error (see Experimental Section for method of determination).
 (55) A study submitted from this laboratory (D. Z. Rogers and T. C. Bruice) will shed some light on this question.

Oxidation of Amines with Sulfonyl Peroxides. 5. Base-Promoted, Imine-Forming Eliminations in *N*-Benzyl-*O*-arylsulfonylhydroxylamines Produced from Benzylamines and Sulfonyl Peroxides

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Abstract: The reactions of substituted benzylamines with substituted arylsulfonyl peroxides give a series of *O*-sulfonylhydroxylamines, $XC_6H_4CH_2NHOSO_2C_6H_4Y$, which undergo base-induced elimination to the imine. By suitable choice of amine and peroxide, substituent effects on the benzylic position and on the leaving group were determined, kinetic deuterium isotope effects were measured, and activation parameters were obtained for imine-forming elimination. The results are best interpreted in terms of an elimination transition state in which leaving group loss is well ahead of benzylic proton removal. The present results are compared with other imine-forming eliminations and with olefin-forming eliminations. The respective transition states are well-accommodated by utilizing a More O'Ferrall-Jencks diagram to depict bonding changes from one system to another.

Introduction

Olefin-forming 1,2-elimination reactions have been studied extensively, and a rather detailed qualitative understanding of steric and electronic effects on these reactions has evolved.² In contrast, if one excludes the acid-catalyzed reactions of carbinolamines,³ 1,2-eliminations to give carbon-nitrogen double bonds have received very little attention. Nitrogen-substituted amines (haloamines, *N*-tosyloxy derivatives) are known to undergo facile elimination to the imine,⁴ and several synthetic procedures for oxidative deamination have attempted to exploit this facility.⁵

Until recently, virtually no mechanistic studies of these systems had been reported. Brauman and Hill reported that *N,N*-difluoroalkylamines undergo elimination in aqueous diglyme, the water being sufficiently basic to promote the elimination (eq 1).⁶ Reactivities and activation parameters were presented, but several traditional methods for studying eliminations (substituent effects, isotope effects, etc.) were not included. Oae and Sakurai investigated the formation of imines from *N*-benzyloxydibenzylamines and weak bases (azide, chloride, and cyanide) in Me_2SO (eq 2).⁷ Negligible substituent effects were observed ($X = H, p-CH_3, p-Cl$) but a large

Table I. Second-Order Rate Constants (k_2) for ($M^{-1} s^{-1}$) Elimination in *O*-Sulfonylhydroxylamines from Substituted Benzylamines **4a-f** and Arylsulfonyl Peroxides **2a-d** in THF-Ethyl Acetate-H₂O

amine	peroxide				
	2a	2b	2c	2d	2e
4a	8.69×10^{-3}	4.53×10^{-3}	1.86×10^{-3}	7.50×10^{-4}	7.99×10^{-3}
4b	7.39×10^{-3}	3.56×10^{-3}	1.14×10^{-3}	5.97×10^{-4}	
4c	7.94×10^{-3}				
4d	1.17×10^{-2}	6.51×10^{-3}	2.43×10^{-3}	1.22×10^{-3}	
4e	1.50×10^{-2}				
4f	1.54×10^{-2}	9.03×10^{-3}	3.23×10^{-3}	1.84×10^{-3}	

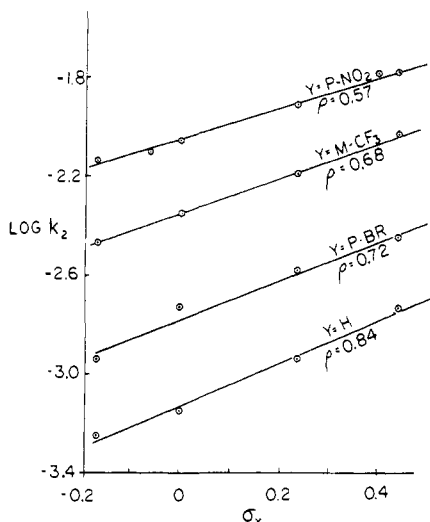
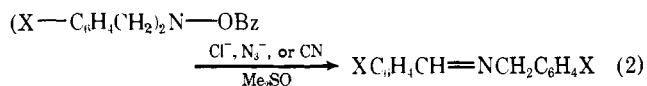
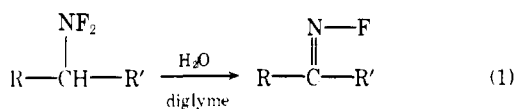
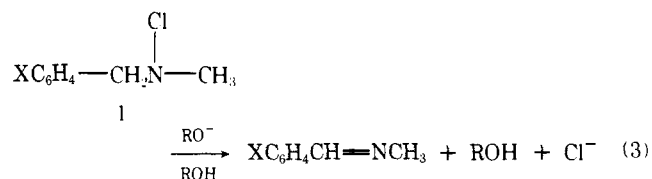


Figure 1. Hammett plots for the base-promoted eliminations, $XC_6H_4CH_2NHOSO_2C_6H_4Y + 4a \rightarrow XC_6H_4CH=NH$. The ρ values obtained for various Y substituents reflect the charge development at the benzylic position.



primary deuterium isotope effect $k_H/k_D = 8.1$ was measured with Cl^- . An E2 type of mechanism was formulated.

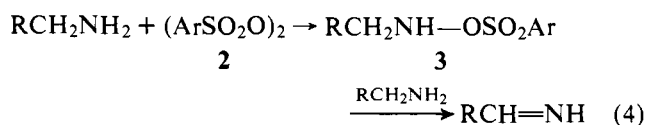
Very recently Bartsch and Cho presented a study of imine-forming 1,2-eliminations in chloramines **1** promoted by alkoxide bases (eq 3).⁸ Substituent effects, isotope effects, base



effects, and activation parameters were compared with analogous olefin-forming dehydrohalogenations of 2-halo-1-arylpropanes. The results were interpreted in terms of a E2 type of transition state with appreciable C-H and N-Cl bond cleavage, little carbanionic character, but significant π -bond formation.

We had earlier observed that the reaction of arylsulfonyl peroxides **2** with amines produced imines.⁹ This conversion involves the rapid formation of an *O*-sulfonylhydroxylamine adduct **3** followed by a slower, base-promoted bimolecular elimination to the imine (eq 4). A two-step, two-electron

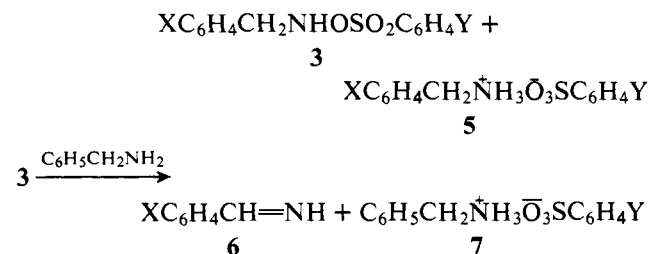
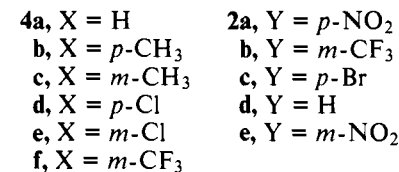
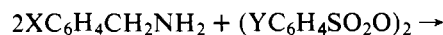
pathway was confirmed by reactivity studies, the molecularity,¹⁰ and cationic rearrangements in suitable amine substrates.^{1a,11} A conductometric technique was used to study the kinetics of the imine-forming elimination step. From substituent effect data and deuterium kinetic isotope effect data, a late, E2 type transition state was postulated. We had also shown that imines are produced in high yields from these reactions so that the measured kinetics correspond to the imine-forming elimination,¹⁰ not other possible processes.⁷



We wish to present the results of studies which examine the transition-state structure from several perspectives, and which give greater insight into structural effects on the elimination reaction.

Results

A series of substituted benzylamines **4a-f** (3 equiv) in 3 M H₂O:THF was reacted at -10°C with a series of arylsulfonyl peroxides **2a-d** (1 equiv) in ethyl acetate for a few minutes. This permitted the formation of the *O*-sulfonylhydroxylamine



adduct **3** and the benzylammonium salt **5**, but there was insufficient excess base present to induce elimination at any measurable rate.¹² A large excess of **4a** was added (50–75 equiv) and the rate of elimination to imine **6** was measured by noting an increase in conductance due to the formation of the benzylammonium salt **7**. Plots of conductance data vs. time were linear throughout the period of measurement (usually >2 half-lives) and the slopes of these plots gave k_{obsd} , the pseudo-first-order rate constant. Since we had shown earlier that the elimination is strictly first order in amine,¹⁰ second-order rate constants were calculated from k_{obsd} and the amine concentration. Very good reproducibility was noted in all cases. The results of these studies are given in Table I. Hammett plots of the rate constants vs. the σ values for the benzylamine substituents are shown in Figure 1 ($r > 0.99$ in all cases). It

Table II. Deuterium Kinetic Isotope Effects k_H/k_D for Eliminations in *O*-Sulfonylhydroxylamines

amine	peroxide		
	2a	2b	2d
4a	4.2	4.2	4.4
4f	5.0		

should be noted that the ρ value for the benzylic carbon is positive and increases steadily as the leaving group becomes poorer.

Furthermore, if the rate constants for elimination in the reactions of benzylamine, **4a**, with arylsulfonyl peroxides **2a–e** are plotted against the σ constants for the peroxide substituents, a ρ value of 1.36 ($r = 0.98$) is obtained. This value is indicative of significant charge development on the leaving group in the transition state.

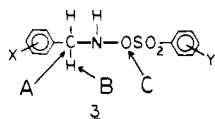
Benzylamine- α,α - d_2 and *m*-trifluoromethylbenzylamine- α,α - d_2 were used to determine the primary kinetic isotope effect values for the benzylic position. Peroxides **2a,b,d** were used with **4a**- α,α - d_2 , and **2a** was used with **4f**- α,α - d_2 . The results are given in Table II.

The rates of elimination for the *O*-sulfonylhydroxylamine adduct **3** from **4a** and peroxides **2a,b,d** were measured over a 30° temperature range (−10 to 20 °C) and the activation parameters were determined. The results, presented in Table III, show that these eliminations have a rather low and invariant activation enthalpy, and a rather large, negative activation entropy. Rate changes for the systems studied are controlled entropically.

The above studies were all conducted in a solvent mixture of 3 M water-THF (15 mL) and ethyl acetate (5 mL) which was ultimately 2.25 M water after mixing. This mixture was originally concocted for several reasons: (a) the amine and peroxide reactants were soluble at −10 °C; (b) the product benzylammonium arylsulfonate salts were soluble at −10 °C; and (c) the conductances of salt solutions were linear with concentration.¹¹ The large negative entropies of activation indicated that strong solvation forces were influential in determining the reaction rate. In order to gauge the effects of solvent on the transition state, 3 M water-THF was used as solvent. Control experiments showed that this solvent also met the criteria discussed above. Rates of elimination in selected systems were measured as before. The derived transition-state parameters are given in Table IV.

Discussion

Transition-State Structure. The use of substituted benzylamines (**4a–f**) and substituted arylsulfonyl peroxides (**2a–e**) allows for a thorough scrutiny of the transition-state structure of the imine-forming elimination in the *O*-sulfonylhydroxylamine adduct **3**. Suitable benzylamine substituents reveal



the extent of charge development on the benzylic position (A); deuterium substitution yields an estimate of C–H bond breaking (B); and different peroxide substituents divulge the extent of charge on the leaving group (C). The activation parameters are indicative of bond-making, bond-breaking changes and of solvation effects. A single base, benzylamine, was used as the promoting base.

The ρ values obtained for the benzylic position are given in Figure 1. The positive sign attests to the development of negative charge on the benzylic carbon in the transition state. The ρ values (0.5–0.8) are of much smaller magnitude than for

Table III. Activation Energies for Base-Induced Elimination in *O*-Sulfonylhydroxylamines ($C_6H_5CH_2NHOSO_2C_6H_4Y$) Derived from Amine **4a** and Peroxides **2a,b,d** in 3 M H_2O :THF:EtOAc

	peroxide		
	2a (Y = <i>p</i> -NO ₂)	2b (Y = <i>m</i> -CF ₃)	2d (Y = H)
ΔH^\ddagger (kcal/mol)	12.0 ± 0.4	12.0 ± 0.1	11.6 ± 0.1
ΔS^\ddagger (eu)	−22.3 ± 1.5	−23.5 ± 0.3	−28.2 ± 0.4
ΔG^\ddagger (kcal/mol)	17.8 ± 0.1	18.2 ± 0.1	19.1 ± 0.1

Table IV. Transition State Parameters for Base-Promoted Eliminations in *O*-Sulfonylhydroxylamines Derived from Amine **4** and Peroxide **2** in 3 M H_2O :THF

entry	amine	peroxide	
1	4a–f	2a	$\rho = 1.20^a$ ($r = 0.99$)
2	4f	2a	$k_H/k_D = 5.7$
3	4a	2a	$\Delta H^\ddagger = 10.9 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -26.6 \pm 0.04$ eu
4	4a	2b	$\Delta H^\ddagger = 11.7 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -24.7 \pm 0.04$ eu

^a ρ value for substituent effect on the benzylic position.

base-induced, styrene-forming eliminations ($\rho \sim 2.0$ – 2.5),¹³ and they are also considerably smaller than the ρ values for alkoxide-induced imine formation in chloroamines ($\rho \sim 1.6$).⁸ The charge development at the benzylic position does change somewhat with leaving group. As the arylsulfonyl substituent changes from *p*-NO₂ to −H, the leaving ability of the sulfonyl group decreases. As the leaving group becomes poorer, the charge density on the benzylic carbon must be larger to help displace the leaving group, and hence a larger ρ is found.

The extent to which the benzylic proton is transferred to the base is indicated by the primary kinetic deuterium isotope effect values shown in Table II. A significant primary isotope effect is observed, indicating that proton removal is important in the transition state. The k_H/k_D values found here are somewhat lower than, but comparable to, base-induced olefin-forming eliminations (PhCD₂CH₂OTs, EtOH/EtO[−], $k_H/k_D = 5.7$)¹⁴ and also alkoxide-induced imine formation in chloramines ($k_H/k_D = 6.4$).⁸ The data are consistent with a transition state with a considerable amount of proton transfer to the base. The k_H/k_D increases from 4.2 to 5.0 as the benzylic protons are made more acidic by a *m*-CF₃ substituent (Table II). Proton transfer must therefore be on the early side of symmetric¹⁵ in the transition state.

By using arylsulfonyl peroxides with varying substituents, the charge development on the leaving group was monitored. By using a Hammett plot of the rate data for amine **4a** with peroxides **2a–e**, the charge development on the leaving group is given by $\rho = 1.36$ ($r = 0.98$). This is a larger value than for most eliminations involving arylsulfonate leaving groups which typically have $\rho \cong 1.0$ ($C_6H_5CH_2CH_2OSO_2C_6H_4Y$, *t*-BuOH/*t*-BuO[−], $\rho = 1.08$).¹³ Therefore, the leaving group is relatively well removed in the transition state.

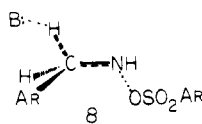
When the component results are combined, a detailed description of the transition state emerges that is best characterized as “unsymmetrical”. The leaving group is well removed and there is substantial benzylic proton removal. However, the lack of benzylic charge development implies that the π bond is well developed in the transition state. The data also support the notion that the transition state is not symmetrical with respect to bonding changes. Loss of leaving group seems to be more advanced than proton removal, and π -bond formation is an important feature of the transition state. In the common spectrum of bimolecular elimination transition-state structures, this could be called an “E1-like” reaction.^{8,16} However, this

Table V. Activation Parameters for Olefin- and Imine-Forming Eliminations

parameter	substrate (reaction conditions) ^e		
	A	B	C
benzylic ρ	~ 2.2 – 2.5^a	$\sim 1.6^b$	0.6–0.8
benzylic k_H/k_D	$\sim 6^c$	$\sim 6.4^b$	4–5
leaving group ρ	$\sim 1.1^d$		1.36
ΔH^\ddagger , kcal/mol	$\sim 20^b$	$\sim 17^b$	~ 12

^a Reference 13. ^b Reference 8. ^c References 14 and 15. ^d Reference 16. ^e A, ArCH₂CH₂OSO₂Ar (RO⁻/ROH); B, ArCH₂N(Cl)CH₃ (RO⁻/ROH); C, ArCH₂NHOSO₂Ar (RNH₂/THF:H₂O:EtOAc).

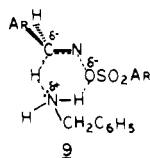
is really an improper description since "E1" implies generation of electron deficiency; in the present case, that electron deficiency would fall on nitrogen. The inability of nitrogen to easily support positive charge¹⁷ renders this description unlikely. A preferred description is skewed—as shown in structure **8**, the



transition state is skewed toward loss of leaving group. (An "E1cB-like" transition state would be skewed toward proton removal.) This avoids an assumption about charge development in the transition state.

The activation parameters for amine-promoted elimination in *O*-sulfonylhydroxylamines are given in Table III. For different arylsulfonate leaving groups, the activation enthalpy remains essentially constant, while the activation entropy becomes more negative with poorer leaving groups. The progression of uncharged reactants to charged products requires that the transition state be more polar than the reactants. Solvation of the transition state demands increased solvent organization and hence a loss of entropy at the transition state.^{6a,18}

Another rationale for the large negative entropy of activation is a syn elimination that features hydrogen bonding between the base and leaving group (**9**). We cannot distinguish



these alternatives at present, although it is clear that the elimination rate is controlled by changes in activation entropy, not enthalpy.

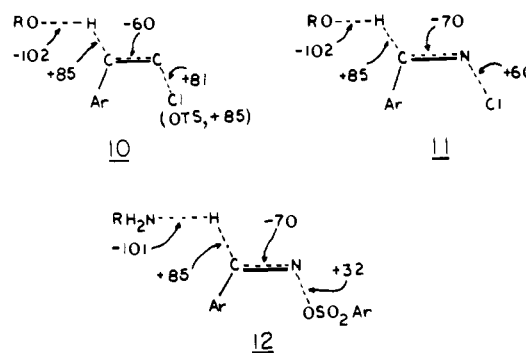
A change to a more polar solvent (3 M H₂O:THF) causes distinct structural changes in the transition state. The polar transition state is better stabilized by solvent and the activation enthalpy decreases (Table IV). A later transition state results with greater proton transfer to base (ρ changes from 0.57 to 1.2, k_H/k_D changes from 5.0 to 5.7) due to an increased solvation of the polar transition state. The stabilizing effects of solvent are countered by a decrease in activation entropy, so that the reaction rate in a more polar solvent is actually slower.

Comparison with Other Bimolecular Eliminations. The data reported here are similar to, but different from, the data on imine-forming eliminations from chloramines reported by Bartsch,⁸ and quite different than analogous olefin-forming eliminations.^{13–16} These are all fundamentally similar reactions inasmuch as they are all bimolecular, base-promoted eliminations; the attachment of the leaving group to nitrogen rather than carbon does not foment any deep-seated change in

mechanism. What are affected, however, are the relative amounts of bond-breaking, bond-making in the various transition states. Olefin-forming eliminations tend to be skewed toward proton removal; the chloramine eliminations tend to have similar amounts of proton removal and leaving group departure;⁸ and *O*-sulfonylhydroxylamine eliminations are skewed toward leaving group loss. Due to the fact that there are large differences in base-solvent systems for the various systems, and due to the complexity of the transition state for base-induced elimination, it is somewhat perilous to make exacting comparisons between such different systems. Nevertheless, Table V recapitulates the tendency of the data to support these descriptions. As one proceeds from left to right by substrate, less change occurs at the benzylic position; more change is associated with the leaving group.

A satisfactory explanation for this trend is related to bond energies in the various reactants. Saunders, in his excellent review, warns that, for a complex process such as bimolecular elimination, prediction of transition state structure based on bond energy changes is very difficult.¹⁹ However, it should be noted that only small bond energy changes (~ 5 – 15 kcal/mol) result from using different bases or leaving groups for the olefin-forming systems.²⁰ With the inclusion of chloramine eliminations⁸ and the *O*-sulfonylhydroxylamine eliminations in the comparison, it is now possible to evaluate the results of large bond energy changes which seem to be much more obvious in effect.

For any elimination promoted by base, there are four bonds involved. As a shorthand method of notation, the bond dissociation energies (BDE) of various bonds are applied to the transition states for elimination.²¹ Negative BDE's (kcal/mol) refer to bonds being made; positive BDE's (kcal/mol) refer to bonds being broken in the reaction. For the systems under comparison, it is evident that major bond energy differences concern π -bond formation and loss of leaving group; energy changes for proton removal should be nearly constant. Further, the greatest change relates to the bond strength to the leaving group which gets significantly weaker from **10** to **12**.²² The



steadily decreasing activation enthalpies across the series (Table V) reflect these bond energy changes.

The ΔH^\ddagger changes relate to an earlier (**12**) or later (**10**) description of the transition state along the reaction coordinate of a More O'Ferrall-Jencks diagram (Figure 2).²³ This is typical "Hammond effect" behavior. Superimposed upon this diagonal transition state positioning are the changes in relative bond strengths of the various transition states **10**–**12**. The weaker N–O bond in **12** results in a shift of the transition state toward the upper left corner (*'12). The dotted curve passing through *'12 represents the new reaction coordinate and the transition state for this reaction coordinate is skewed toward the loss of leaving group (more L–X cleavage, less C–H cleavage, more π -bond formation).

For olefin-forming elimination, the greater strength of the L–X bond should cause a shift in the transition state toward the lower right corner (*'10). The dotted curve through *'10

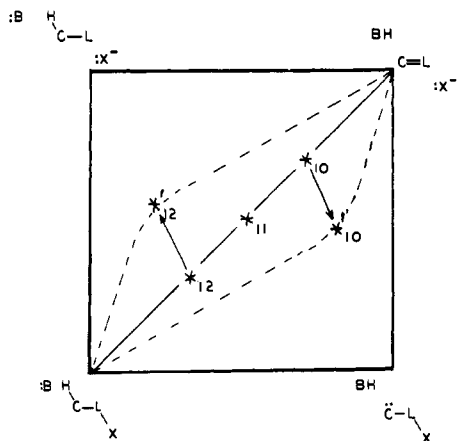


Figure 2. More O'Ferrall-Jencks diagram²³ for base-catalyzed eliminations where L, the site of leaving group attachment, is either carbon or nitrogen. The diagonal represents the totally synchronous progression of reactants (lower left) to products (upper right). Positioning of transition states (*₁₀₋₁₂) along this diagonal is dictated by the Hammond postulate. Shifts away from the diagonal (*₁₂ → *₁₁) are changes in transition-state structure predicted by Thornton's rules.²³

represents the reaction coordinate for olefin-forming elimination whose transition state is skewed toward proton loss (more C-H cleavage, less L-X cleavage, less π -bond formation). The magnitudes of the perpendicular shifts shown in Figure 2 are only indicative of the direction of transition-state change.

The use of More O'Ferrall-Jencks diagrams to describe changes in transition state structure is a very useful method. However, for the base-promoted eliminations discussed here, only qualitative use may be made of these diagrams. The problem resides in the fact that only two-bond length parameters are used to describe a transition state in which four bonds are involved.^{24a} In addition, charge development in the transition state is not necessarily synchronous with bond cleavage.^{24b} Therefore, the several parameters used to define the transition state (ρ values, isotope effects, etc.) are only qualitatively related, and they cannot be quantitatively pictured in a single diagram.

There are, however, sufficiently large differences for olefin- and imine-forming eliminations, that such diagrams can properly predict structural differences in the respective transition states. Furthermore, it is hoped that *O*-sulfonylhydroxylamines are sufficiently reactive that other transition state probes (Bronsted studies, for example) can be used in an attempt to quantify the position of the transition state. We hope to study these elimination types under more experimentally similar conditions in order to test the mechanistic conclusions more cleanly.

Experimental Section

Reagents. Amines **4a-f** and the deuterated amines **4a- α,α -d₂** and **4f- α,α -d₂** were prepared as described previously.¹⁰ Arylsulfonyl peroxides **2a-e** were prepared according to the procedures of Dannley²⁵ (**2a,b,e**) and Kergomard²⁶ (**2c,d**). Solvents were purified as described previously.¹⁰

Kinetic Procedure. The apparatus used to obtain conductance data has been detailed earlier.¹⁰ Kinetic runs were carried out as follows.

A solution of a sulfonyl peroxide in ethyl acetate (0.003 M) was equilibrated at the reaction temperature (normally -10.0 ± 0.05 °C), and 5.0 mL was transferred by pipet into the conductivity cell. Addition of 15.0 mL of a 3 M H₂O:THF solution, also equilibrated at the reaction temperature, gave a 7.5×10^{-4} M peroxide solution. A substituted benzylamine (0.045 mmol, 3 equiv) was added by syringe and the mixture was shaken from 1 to 5 min to complete the formation of the *O*-sulfonyl-*N*-benzylhydroxylamine intermediate **3**. After this

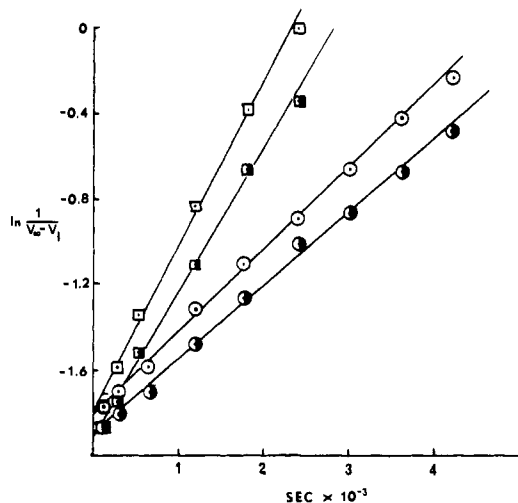


Figure 3. Typical kinetic plots of conductance data¹⁰ vs. time for benzylamine-promoted elimination in *O*-sulfonylhydroxylamine adducts from **4b** and **2a** (circles) and **4f** and **2a** (squares). For the adduct from **4b** and **2a**, the benzylamine concentrations were 0.0449 M (●) and 0.0499 M (○) and gave second-order rate constants of 7.34×10^{-3} and 7.45×10^{-3} M⁻¹ s⁻¹, respectively. For the adduct from **4f** and **2a**, the promoting amine concentrations were 0.0419 M (◻) and 0.0503 M (◻) and gave second-order rate constants of 1.53×10^{-2} and 1.54×10^{-2} M⁻¹ s⁻¹, respectively.

period no further change in the conductance could be observed indicating that adduct formation was complete, but elimination was too slow to measure. The elimination was initiated by adding benzylamine (approximately 1 mmol, 50–70 equiv) and the increase in conductance with time was observed. The precise amount of added benzylamine **4a** was used to calculate the final amine concentration. From the conductance data, the pseudo-first-order rate constants were extracted¹⁰ and hence the second-order constants (k_2) after division by the amine concentrations. All rate constants reported are the average of at least two runs, and kinetic runs usually agreed to within $\pm 2\%$. Some typical kinetic results are shown in Figure 3. It was noted that, when new batches of solvent were prepared, rate constants would sometimes vary systematically higher or lower. For example, amine **4a** with peroxide **2c** gave rate constants of 4.53×10^{-3} and 4.11×10^{-3} M⁻¹ s⁻¹ for two different solvent batches. These differences, although small, are quite reproducible. Therefore for each series of reactions, a single batch of solvent was used for all substrates. The origin of these slight rate changes is quite unknown.²⁷

Activation parameters were obtained by carrying out the kinetic measurements at several temperatures spanning a 30 °C range, and then calculating the activation parameters.

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References and Notes

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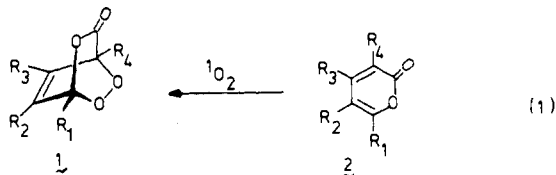
α -Pyrone Endoperoxides. Synthesis, Thermal Decomposition, and Chemiluminescence¹

Waldemar Adam*² and Ihsan Erden

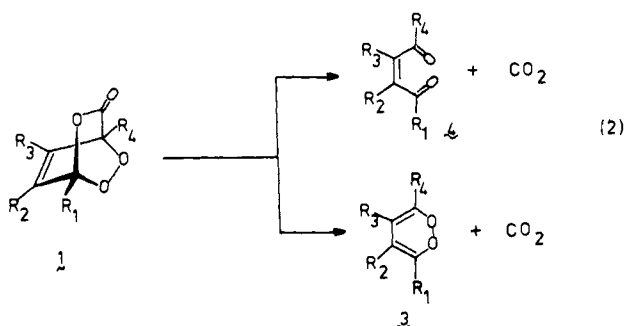
Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. Received February 9, 1979

Abstract: Singlet oxygenation of α -pyrones **2** affords the corresponding endoperoxides **1** in high yield. On heating, these peroxides quantitatively decarboxylate into the respective 1,2-diacetylenes **4**. The suspected intermediary *o*-dioxins **3** could not be trapped with maleic anhydride, tetracyanoethylene, and *N*-phenyl-1,2,4-triazoline-3,5-dione, suggesting that the decarboxylation of the endoperoxides **1** takes place with concomitant peroxide bond fission. Easily oxidized polycyclic aromatic hydrocarbons, e.g., rubrene, perylene, and 9,10-diphenylanthracene, induce the decarboxylation of the endoperoxides **1** with light emission by an electron exchange mechanism.

α -Pyrone endoperoxides **1**, conveniently accessible through singlet oxygenation of α -pyrones **2** (eq 1),³ are po-

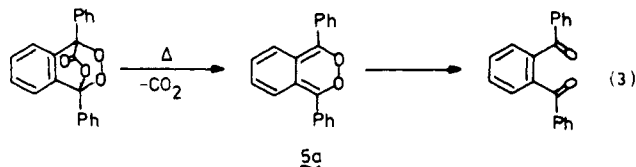


tential sources for the thermal generation of electronic excitation.⁴ Indeed, even a very rudimentary estimate⁵ of the enthalpy change associated with the thermal decarboxylation of **1** into the diacetylene **4**, as shown in eq 2, reveals that



enough energy is set free in the **1** \rightarrow **4** process to render **4** electronically excited. Our preliminary observations³ confirmed that the α -pyrone endoperoxides **1** are hyperenergetic in that chemiluminescence accompanied their thermal decarboxylation.

In the course of our more detailed investigation of these functionalized endoperoxides, a preliminary report by Smith and Schuster⁶ focused on a still more fascinating aspect of this problem. Thus, thermal decomposition of 1,4-diphenyl-2-benzopyran-3-one endoperoxide led to the novel *o*-xylylene peroxide **5a** (eq 3), which subsequently rearranged into elec-



tronically excited *o*-dibenzoylbenzene. The unusual feature of this chemielectronic process is that decarboxylation preserves the peroxide linkage in the form of the 1,2-dioxin moiety in the xylylene peroxide **5a**. An analogous process was first suggested by Michl⁷ to rationalize the chemiluminescence of luminol, in which the postulated endoperoxide **6** loses molecular nitrogen with preservation of the peroxide linkage to afford the xylylene peroxide **5b** (eq 4). The latter affords electroni-