Notes

Steric Effects in the Quenching of Aromatic Ketone Phosphorescence: Tetraisopropylethylene

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Tetraisopropylethylene [TIE] is a sterically very hindered alkene. The isopropyl groups are twisted into a picket fence array and thus protect the double bond from electrophilic attack.[1] A second consequence of this conformation is that the allylic CH bonds all lie in the plane of the carbon–carbon double bond. Models suggest that they too are sheltered from attack.

One of the ways that one can assess the reactivity of a sterically hindered alkene is to measure its reactivity as a quencher of aromatic ketone phosphorescence in solution.[2] Those ketones whose phosphorescence is readily observable have lowest ($n\pi^*$) triplet states. The alkene acts as an electron donor, giving the reaction some of the characteristics of electrophilic attack on the alkene. In this paper we report the rate constants and activation parameters for the quenching by TIE in carbon tetrachloride solution of the phosphorescence of 4-(methoxycarbonyl)benzophenone (1). This quenching is substantially slower and less efficient than that by other tetraalkylethylenes such as tetramethylethylene and adamantylideneadamantane.

Rate constants k_{ir} for the process [1^{*3} + TIE $\rightarrow$ quenching products] were obtained from phosphorescence lifetime measurements, where τ is the lifetime of 1^{*3} in the presence of quencher and τ_0 is the lifetime in the absence of quencher. The data were fit to the modified Stern–Volmer expression

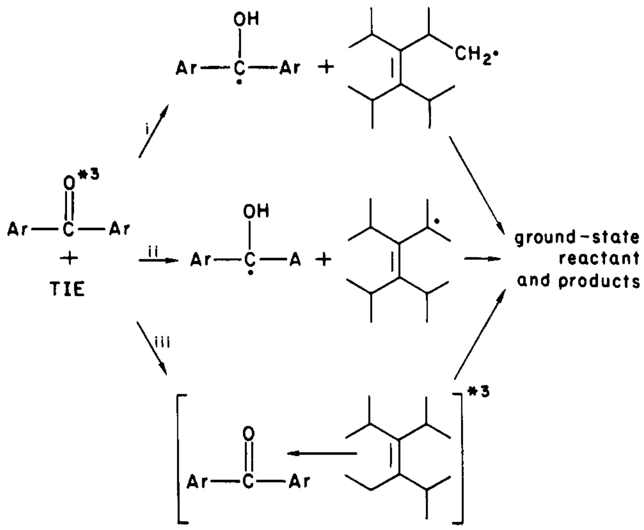
$$1/\tau = 1/\tau_0 + k_{ir}[\mathrm{TIE}] \qquad (1)$$

Values for k_{ir} were obtained in the temperature range −20 °C to 150 °C.

Dilute solutions (1.5×10^{-3} M) of 1 in CCl_4 together with five different concentrations of added tetraisopropylethylene (up to 1×10^{-2} M) were prepared and degassed by five successive freeze–pump–thaw cycles on a vacuum line. The phosphorescence lifetimes of 1 in the six samples were measured by flash photolysis[3,4] and lifetimes in the range 30–80 μs at room temperature were obtained. Two identical sets of six samples were made up. Using a six-sample constant temperature block,[1] k_{ir} was obtained for one sample set at many temperatures ascending the temperature scale and the other set decending the temperature scale. The k_{ir} values for each sample set were treated in an Arrhenius fashion to obtain the activation energies and preexponential factors.[4]

The following parameters were obtained: $k_{ir}^{25\,°C} = (1.6 \pm 0.5) \times 10^6\ M^{-1}\ s^{-1}$, $E_a = 2.7 \pm 0.2$ kcal/mol, $A = (1.3 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$.

Scheme I



There are three mechanisms which can account for the quenching of 1^{*3} by TIE (Scheme I). These are (i) H abstraction from the methyl groups, (ii) H abstraction of an allylic hydrogen, and (iii) exciplex formation between the excited ketone and the olefinic double bond. Mechanism i can be discounted by a simple calculation. Primary H abstraction occurs with a rate constant of ca. $4 \times 10^3\ M^{-1}\ s^{-1}$ per hydrogen at room temperature.[5] Thus this reaction for tetraisopropylethylene would have a rate constant of ca. $1 \times 10^5\ M^{-1}\ s^{-1}$ (for the 24 primary hydrogens) which is only about 6% of the observed rate constant. Also the activation energy observed in this reaction (2.7 kcal/mol) is much lower than the activation energy for primary H abstraction by triplet benzophenone (4.4 kcal/mol).[5]

There is substantial evidence showing that the excited states of ketones when quenched by electron-rich alkenes do so via the exciplex mechanism[4,6] with rate constants much larger than those for hydrogen abstraction reactions. For example, the analogous unhindered alkene tetramethylethylene quenches 1^{*3} with a rate constant of $1 \times 10^9\ M^{-1}\ s^{-1}$ whereas quenching by a secondary CH_2 group occurs with $k_{ir} = 1 \times 10^5\ M^{-1}\ s^{-1}$. Previous studies[2] have shown that steric hindrance on the alkene causes a lowered k_{ir} (for mechanism iii) which is usually due to an increased activation energy but no change in A factor. Adamantylideneadamantane, an extremely hindered tetrasubstituted alkene, has $k_{ir} = 1.5 \times 10^8\ M^{-1}\ s^{-1}$ with the lower reactivity due to an increase in E_a from 0.15 kcal/mol for tetramethylethylene to 2.1 kcal/mol. Surprisingly, tetraisopropylethylene shows an even greater drop in k_{ir} (= $1.5 \times 10^6\ M^{-1}\ s^{-1}$), part of which is due to an increased E_a (=

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2.7 kcal/mol). This quencher behaves somewhat differently than adamantylideneadamantane in that a reduced *A* factor accounts for at least 20-fold decrease in k_{ir}. A reduced *A* factor due to steric hindrance has also been observed in *cis*-1,2-di-*tert*-butylethylene.[2]

The allylic character of the tertiary C–H bonds presumably contributes little to their reactivity in TIE, since the molecular geometry would minimize any allylic resonance stabilization of the carbon-centered radical. On the other hand, formation of a planar tertiary radical would be accompanied by some reduction in unfavorable CH_3/CH_3 interactions. A good model for this reaction is not available, although the rate constants, *A* factor, and activation energy determined are not at odds with abstraction of a tertiary hydrogen. Our results are thus consistent with quenching via tertiary hydrogen abstraction or via exciplex formation. If more TIE were available, product studies and flash absorption studies would yield further information on the reaction intermediates.

Conclusion

We have studied the triplet state quenching of an aromatic ketone by tetraisopropylethylene. It is substantially less reactive than other tetrasubstituted alkenes. The rate and activation parameters can be explained either by an exciplex quenching mechanism or by tertiary hydrogen abstraction. Which ever mechanism dominates, it is clear that the steric hindrance of four isopropyl groups on a double bond causes a decrease in its reaction rate with the excited ketone to be at least 1000 times slower than tetramethylethylene and 100 times slower than adamantylideneadamantane.

Experimental Section

TIE was a gift from Professor Y. Okamoto of the Polytechnic Institute of New York. Sets of six solutions were prepared containing 1.5×10^{-3} M 4-(methoxycarbonyl)benzophenone in carefully purified CCl_4[4] and concentrations of TIE ranging from zero to 1×10^{-2} M. Aliquots (2 mL) in 13 mm o.d. Pyrex tubes were degassed on a vacuum line by five successive freeze–pump–thaw cycles and sealed under vacuum. Samples were excited with 10-ns pulses from a nitrogen laser. Emission was detected at right angles, as previously described,[4] with the transient signal digitized with a Biomation Model 8100 wave form recorder. Data were fit to a single exponential form and lifetimes were plotted according to eq 1 to obtain rate constants.

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Registry No. 1, 6158-54-9; TIE, 7090-88-2; tetramethylethylene, 563-79-1; adamantylidene adamantane, 30541-56-1.

Deoxygenation of Sulfoxides with Boron Bromide Reagents

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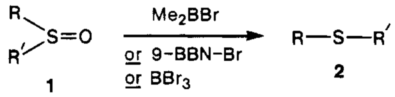
The growing importance of organosulfur compounds in organic synthesis has recently stimulated the development of numerous useful methods for the deoxygenation of sulfoxides to sulfides.[1] For example, hydrogen halides have been used for this purpose although their usefulness is somewhat restricted with acid-sensitive substrates.[2] Other methods have successfully utilized strong oxygenophiles such as trivalent phosphorus in order to activate the oxygen–sulfur bond.[3] However, in most cases the reaction requires the use of elevated reaction temperatures and/or prolonged reaction times. Reduction by hydrides ($LiAlH_4$–$TiCl_4$[4]; $NaBH_4$–$CoCl_2$[5]) has attracted some attention, but their strong reducing character represents a limitation. Acylating agents alone or in combination with reducing agents such as I^- have been used successfully, but the reactivity of these agents with a number of functionalities imposes certain limitations on their usefulness.[6]

Scheme I



Recently, trimethylsilyl halides (Me_3SiI, Me_3SiBr) have been reported to reduce dialkyl sulfoxides to sulfides rapidly at room temperature.[7] Deoxygenation of dibenzyl sulfoxides, however, resulted in a mixture of halogenated dibenzyl sulfides. This problem was very effectively solved by the use of (trichloromethyl)silane in the presence of sodium iodide at room temperature.[8]

Among boron reagents, dichloroborane is the only discrete boron derivative which, to our knowledge, has been used successfully for the deoxygenation of sulfoxides.[9] Although dichloroborane reacts readily with dialkyl sulfoxides, the reduction of diaryl sulfoxides requires much longer reaction times, thus reducing somewhat the general usefulness of this reagent.

Recently we reported that dimethylboron bromide efficiently cleaves cyclic and acyclic acetals and ketals including MEM ((2-methoxyethoxy)methyl), MOM (methoxymethyl), and MTM (methylthiomethyl) ethers at −78 °C, as well as a variety of alkyl methyl, aryl methyl, cyclic, and THP ethers at room temperature.[10] Attracted by the powerful oxygenophilic character of this reagent, coupled with our interest in sulfur chemistry,[11] we decided to investigate its reactivity with sulfoxides. As a result we are gratified to report herein that dimethylboron bromide, 9-borabicyclo[3.3.1]nonyl bromide (9-BBN-Br) and boron

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