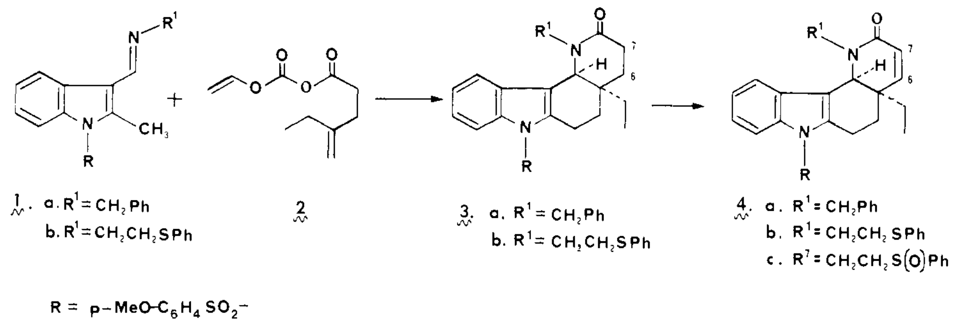
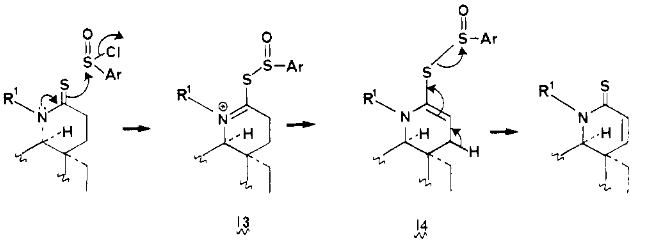
Scheme I



Scheme II



(MeI/THF/50 °C/4 h; $NaBH_4$/MeOH/25 °C)[4] gave the allylic amine **7** (52%, mp 72–76 °C).

The thiolactam **5b** was readily dehydrogenated (*p*-TolS(O)-Cl/CH_2Cl_2/0 °C to room temperature/6 h) to give **6b** (81%, mp 183–185 °C). The α,β-unsaturated thiolactam was converted into the α,β-unsaturated lactam **4b** under nonoxidative conditions by treatment with $Et_3O^+BF_4^-$ (CH_2Cl_2/25 °C) and subsequent hydrolysis (KOH/H_2O/THF/25 °C). Conversion of **4b** into **4c** (*m*-CPBA/CH_2Cl_2/H_2O/$NaHCO_3$) followed by intramolecular Pummerer reaction (TFAA/PhCl/135 °C) gave the pentacyclic system **8** (65%, mp 203–207 °C). We were unable to desulfurize **8** (in attempts to prepare **9**) using a variety of Raney nickel catalysts without hydrogenating the enone double bond. We therefore changed the order of the reactions above.

Extension of the thiolactam dehydrogenation to the pentacyclic system **10** was readily achieved. Conversion of **10** into the thiolactam **11** was carried out using the Lawesson reagent (toluene/90 °C/2.5 h; 73%, mp 189–190 °C). When the thiolactam **11** was treated with *p*-TolS(O)Cl (CH_2Cl_2/N-*i*-Pr_2Et/65 °C; HOAc/H_2O/25 °C) it was cleanly converted into the α,β-unsaturated thiolactam **12** (92%, mp 166–168 °C). Treatment of **12** with Meerwein's salt ($Et_3O^+BF_4^-$/CH_2Cl_2/25 °C) followed by hydrolysis (KOH/H_2O/THF/25 °C) gave the pentacyclic unsaturated lactam **9** (80%, mp 168–171 °C).

At present we believe that the mechanism of this extremely mild thiolactam dehydrogenation involves phenylsulfinylation on sulfur to give the thioiminium ion **13** (Scheme II). Proton loss to give **14**, followed by 1,4-elimination leads to the α,β-unsaturated thiolactam.[5] We discount the usual α-phenyl sulfoxide followed by syn elimination since the conditions for such a process are not compatible with the mild reaction conditions. It should be noted that the application of this new procedure has not yet been extended to other systems, and our present evidence indicates that the steric and electronic environment of the nitrogen atom plays an important part in determining whether or not the dehydrogenation works.[6] Despite these present, general limitations, this mild new method provides a high yielding way to introduce the 6,7-double bond into Aspidosperma type alkaloids.[7]

Acknowledgment. The National Institutes of Health (GM 29802) are thanked for their financial support. The National Science Foundation (CHE 81-05004) is thanked for funds to purchase a 360-MHz NMR spectrometer.

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(4) Raucher, S.; Klein, P. *Tetrahedron Lett.* **1980**, 4061. Sundberg, R. J.; Walters, C. P.; Bloom, J. D. *J. Org. Chem.* **1981**, *46*, 3730.

(5) For reaction of *sec*-thioamides with sulfinylating agents, see: Walter, W.; Hell, P.-M. *Liebigs Ann. Chem.* **1969**, *727*, 50. Chabrier, P.; Renard, S. H. *Bull. Soc. Chim. Fr.* **1949**, 272. Hurd, R. N.; De La Mater, G. *Chem. Rev.* **1961**, *61*, 45. Walter, W.; Hell, P.-M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 696.

(6) The chemistry of the RSS(O)R functional group has been studied: Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *J. Org. Chem.* **1982**, **47**, 3403. Pyrolysis of dibenzyl thiosulfinate gave thiobenzaldehyde and phenylmethanesulfenic acid. Baldwin, J. E.; Lopez, R. C. G. *J. Chem. Soc. Chem. Commun.* **1982**, 1029.

(7) All new compounds described here gave microanalytical data (C, H, N), IR, and ^1H NMR (360 MHz) consistent with the assigned structure and elemental composition.

Hydrogen Atom Transfer Reactions: The Nature of the Transition State As Delineated from the Temperature Dependence of the Primary KIE[1]

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Because hydrogen atom transfer reactions are among the simplest of all bond-making–bond-breaking processes, their study has been and remains a matter of theoretical as well as general interest. Johnston and co-workers,[2] for example, have studied extensively the gas-phase reaction

$$F_3C\cdot + CH_4 \rightarrow F_3CH + H_3C\cdot$$

and find that a substantial correction for tunneling is required (k_H/k_D > 15 at 80 °C). Investigations of similar processes in solution have been less extensive. Thus, both Pryor[3] and Lewis[4] studied the reaction

$$R\cdot + R'SH \rightarrow RH + R'S\cdot$$

and found a rough correlation between the magnitude of the kinetic isotope effect and the heat of reaction, $\Delta H°$; however, no single internally consistent plot of KIE vs. $\Delta H°$ was observed. Two opposing factors were suggested to account for this failure: (1) steric repulsion in the transition state resulting in an increase in activation energy and (2) the reduction in activation energy caused by polar contributions to the structure of the transition state. In a related study,[5] the attack of a variety of carbon radicals on tri-*n*-butyltin hydride was examined, but few meaningful conclusions were drawn.

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(1) Supported by the NSF, Grant CHE 80-17045.

(2) Johnston, H. S. "Gas Phase Reaction Rate Theory"; Ronald Press: New York, 1966.

(3) Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584.

(4) Lewis, E. S.; Ogino, K. *J. Am. Chem. Soc.* **1976**, *98*, 2260.

(5) Kozuka, S.; Lewis, E. *J. Am. Chem. Soc.* **1976**, *98*, 2254.

0002-7863/83/1505-6526$01.50/0

Table I. KIE Parameters Associated with H Atom Transfer from $(n\text{-}C_4H_9)_3SnH(D)$ to Various Carbon Radicals in Decane[a]

entry	R-X	temp, °C[b]	k_H/k_D[c]	$[\Delta E]_H^D$, kcal/mol	A_H/A_D	r[d]
1	$CH_3(CH_2)_6CH_2Cl$	60.3	1.883	0.303 ± 0.017	1.20	0.994
		70.1	1.866			
		80.4	1.844			
		90.1	1.823			
		109.8	1.776			
2	$CH_3(CH_2)_6CH_2Br$	20.4	2.034	0.364 ± 0.019	1.09	0.994
		40.1	1.960			
		80.5	1.808			
		101.4	1.769			
		121.5	1.746			
3	$CH_3(CH_2)_6CH_2I$	61.8	1.832	0.326 ± 0.012	1.12	0.997
		80.5	1.785			
		90.8	1.767			
		97.8	1.745			
		100.1	1.742			
4	$CH_3(CH_2)_5(CH_3)CHBr$	56.0	2.036	0.466 ± 0.025	0.996	0.995
		65.4	1.986			
		74.9	1.952			
		85.2	1.920			
5	$CH_3(CH_2)_2C(CH_3)_2CH_2Br$	29.9	1.884	0.314 ± 0.034	1.11	0.990
		49.9	1.839			
		69.9	1.771			
6	$(CH_3CH_2)_2(CH_3)CBr$	20.5	1.997	0.304 ± 0.09	1.19	0.999
		39.0	1.939			
		60.8	1.870			
		80.0	1.831			
7	C_6H_5Br	40.2	1.408	≈0	1.40	0.999
		50.1	1.396			
		59.4	1.408			
		69.4	1.414			
		78.1	1.408			
8	$C_6H_5CH_2Br$	42.0	2.689[e]	0.754 ± 0.042	0.810	0.994
		55.0	2.610			
		70.0	2.418			
		94.7	2.280			
		109.4	2.184			
9	$p\text{-}FC_6H_4CH_2Br$	39.9	2.661[e]	0.756 ± 0.030	0.794	0.997
		54.2	2.550			
		70.1	2.417			
		100.1	2.191			
10	$p\text{-}CF_3C_6H_4CH_2Br$	20.4	2.795[e]	0.655 ± 0.003	0.908	0.999
		60.5	2.444			
		101.6	2.187			
		121.6	2.098			
11	$p\text{-}CH_3C_6H_4CH_2Cl$	40.1	2.936[e]	0.808 ± 0.009	0.802	0.999
		60.8	2.713			
		80.9	2.540			
		121.5	2.245			

[a] Initial composition: [RX] = 0.069 M; $[n\text{-}Bu_3SnH] \simeq [n\text{-}Bu_3SnD] = 0.69$ M. All reactions were initiated with AIBN (~0.1%). [b] A constant (±0.02 °C) temperature was maintained throughout the course of each reaction. [c] The primary hydrogen–deuterium isotope effect, determined competitively, can be expressed as $k_H/k_D = ([n\text{-}Bu_3SnD]/[n\text{-}Bu_3SnH])([RH]/[RD])$. The former ratio, $[n\text{-}Bu_3SnD]/[n\text{-}Bu_3SnH]$, is equal to the ratio of $[n\text{-octane-}d_1]/[n\text{-octane-}d_0]$ resulting from the reaction of $n\text{-}Bu_3SnH\text{–}n\text{-}Bu_3SnD$ with an excess of *n*-octyl bromide. For those reactions carried out at temperatures <40 °C, initiation was assisted by the use of UV irradiation. The isotopic composition of the isolated octane was determined by high-precision, whole-molecule mass spectrometry, employing a total of ca. 4000 scans while simultaneously monitoring the M, M + 1, and M + 2 ions. High-precision, whole-molecule mass spectrometry was also employed to determine the ratio [RH]/[RD]. Unless otherwise indicated, an ionizing voltage of 70 eV and a constant source pressure of between 6×10^{-7} and 8.0×10^{-7} mmHg were employed. Unless otherwise indicated, no significant (i.e., >1%) M – 1 ion was observed and no correction was applied. [d] Correlation coefficient. [e] These determinations were performed at an ionizing voltage of 11 eV. Under these conditions, the intensity of the M –1 ion was always ≲20% that of the M ion. A recognized literature[12] procedure was employed to correct for this contribution prior to calculating the listed KIE values.

Within the framework of transition-state theory, the temperature dependence of the kinetic isotope effect affords a delicate probe of transition-state qualities. We report here the results of our study of the temperature dependence of the KIE associated with the reduction of a representative series of organic radicals by tri-*n*-butyltin hydride.

$$R\cdot + Bu_3SnH(D) \rightarrow RH(D) + Bu_3Sn\cdot$$

Our findings, summarized in Table I, reveal the following points: First, the observed KIEs are essentially equivalent, as they should be, for RCl, RBr, and RI (cf. entries 1–3).

Second, the value of the preexponential term in all instances falls within the normal range of $0.7 \leq A_H/A_D \leq 2^{1/2}$ and gives no experimental evidence of tunneling.[6]

Third, the transition state for H-atom transfer becomes increasingly unsymmetrical according to the order benzyl < 2° < 1° < phenyl. (The standard or ground-state value for the difference in zero-point energy, $[\Delta E_0]_H^D$, for the Sn–H vs. Sn–D bond in $Bu_3SnH(D)$, as determined from infrared measurements in decane, is 0.74 ± 0.08[7] kcal/mol.) Indeed, it is apparent (Figure 1) that the difference between the difference in zero-point energy of the reactant and the difference in zero-point energy of the

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(6) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980.

(7) Estimated error. The Sn–H bond dissociation energy has been estimated at 70 kcal/mol,[11] significantly less than the lowest value of the bond dissociation energy for benzylic C–H bonds.

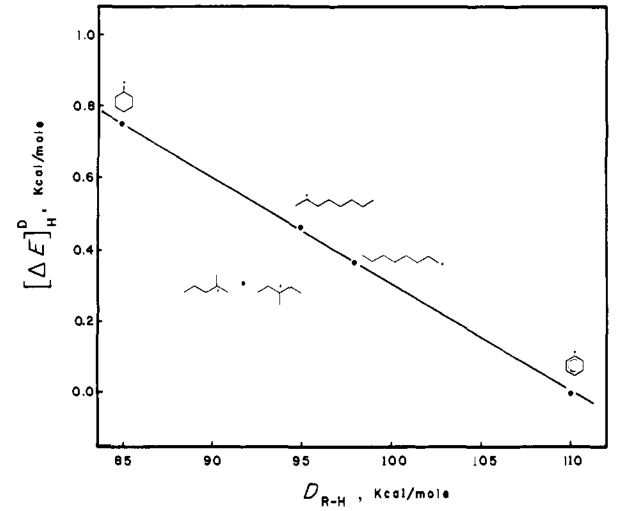

Figure 1. Plot of the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state, $[\Delta E]_H^D$, vs. the bond dissociation energy,[13] D_{R-H}, of the carbon–hydrogen bond formed as a result of the hydrogen atom transfer between R· and n-Bu_3SnH. Those values corresponding to the tertiary systems (entries 5 and 6) are plotted to show the magnitude of their deviation but are ignored in computing the best-fit line.

transition state, i.e., $[\Delta E]_H^D$, is linearly related to the bond energy, D_{R-H}, of the resulting carbon–hydrogen bond (vide infra), the best-fit equation being

$$[\Delta E]_H^D = -0.0302(D_{R-H}) + 3.329 \text{ kcal/mol}$$

This observation provides experimental justification of a fundamental tenet of kinetic isotope theory, viz., that for a linear 3-center hydrogen transfer, the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state is linearly proportional to the heat of the reaction,[8] and sustains earlier suggestions[3,9] of the likelihood of using kinetic isotope effect studies as a means of determining C–H bond energies.

Fourth, this linear correlation fails for the tertiary systems (entries 5 and 6) when, presumably because of increased steric repulsion, the activation energy, E_a, for hydrogen atom transfer is increased, resulting in a less unsymmetrical transition than would have occurred in the absence of such steric effects.

Finally, the influence of polar contributions on the nature of the transition state is revealed in entries 8–11, from which it is apparent that the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state increases as the electron density at the carbon radical center is enhanced. Such contributions can result in substantial differences in bond-dissociation energies: cf. $D(p\text{-}MeOC_6H_4CH_2\text{–}H)$ = 83.5 kcal/mol vs. $D(p\text{-}CF_3C_6H_4CH_2\text{–}H)$ = 88.5 kcal/mol. Thus, within an homologous series, as the transition state for H transfer becomes less symmetrical, i.e., as $[\Delta E]_H^D \rightarrow 0$, radical selectivity will be diminished. As might be expected, this behavior manifests itself in a linear free-energy relationship in the case of benzyl series ($[\Delta E]_H^D$ vs. σ), with a ρ value of −0.189 ($r = 0.996$), the magnitude of which is consistent with the intervention of a free-radical reaction. Collectively, these findings provide strong support for the frequently cited role of polar contributions in determining free-radical reactivity patterns.[14]

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(8) Westheimer, F. *Chem. Rev.* **1961**, *61*, 265.

(9) Lewis, E. S.; Butler, M. M. *Chem. Commun.* **1971**, 941.

(10) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(11) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

(12) Benz, H. *Anal. Chem.* **1980**, *52*, 248.

(13) Values of D_{R-H} are those reported: Chamberlain, G. A.; Wittle, E. *Trans. Faraday Soc.* **1971**, *67*, 2077. Rodgers, A. S.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1967**, *89*, 4578.

(14) Cf.: Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 150–177. Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.

Excited-State Porphyrin–Quinone Interactions at 10-Å Separation

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To investigate the effects of distance and orientation in electron-transfer reactions[1] and to provide a model for a photosynthetic reaction center,[2] we synthesized a molecule (PQ) containing a porphyrin and a quinone held rigidly at a center-to-center distance of 10 Å.[3] The photochemical properties of PQ and its derivatives have now been characterized, using measurements of fluorescence yield and lifetime, delayed fluorescence, and flash photolysis. We report the results of these measurements, which indicate that electron transfer over a distance of 10 Å is the dominant photoreaction in the zinc porphyrin–quinone.

The photochemical properties of PQ are compared with two reference compounds where intramolecular electron-transfer reactions cannot occur. *meso*-Tetrakis[α-*o*-((*p*-anisyl)amino)phenyl]porphyrin (PA_4) has the same substituents as PQ but lacks the quinone, and reduction of PQ gives the porphyrin–hydroquinone PQH_2.

The visible absorption and fluorescence spectra of PQ and PA_4 are identical. The yield of fluorescence emission was identical for PA_4 and PQ, but the fluorescence yield in ZnPQ was only 0.4 of that of $ZnPA_4$, indicating charge transfer from the porphyrin to the quinone in ZnPQ. Further studies were carried out on the amides $ZnPQ(Ac)_4$ and $ZnPA_4(Ac)_4$, in which the aniline groups at the periphery of the porphyrin were acetylated to prevent their oxidation (Figure 1).

The fluorescence yields and lifetimes of $ZnPQ(Ac)_4$ were measured and compared with $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$. The quantum yield of fluorescence in $ZnPQ(Ac)_4$ is 0.011 (by comparison with zinc tetraphenylporphyrin, yield 0.04),[4] and is reduced by 60% in comparison with both $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$. Both of the reference compounds gave single fluorescence lifetimes of 2.2 ns, but $ZnPQ(Ac)_4$ exhibited a biphasic exponential decay of 0.5 and 1.3 ns in a 3:2 ratio (Figure 2). The lifetimes were the same at two emission wavelengths (614 and 660 nm) and two exciting wavelengths (337 and 575 nm), and were constant in the concentration range examined, 10^{-5}–10^{-6} M. The decrease in fluorescence yield and the shortened lifetimes indicate quenching, which we assign to charge transfer from the singlet state of the porphyrin to the quinone,[5] with quantum yield of 60%.

Interaction of the quinone with the porphyrin triplet state was studied by laser flash photolysis at 337 and 347 nm, where the porphyrin absorption is 55 times that of the quinone. Flash photolysis of $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$ gave transients identified as triplet states by their lifetimes ($\tau > 10^{-4}$ s), spectra,[6] and quenching by oxygen. The formation of the triplet state occurred within the response time (30 ns) of the flash photolysis instrument.[7]

The results with $ZnPQ(Ac)_4$ were quite different. In the wavelength region 390–415 nm, a new absorption was found to

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(1) Mauzerall, D.; Ballard, S. G. *Ann. Rev. Phys. Chem.* **1982**, *33*, 377–407.

(2) Clayton, R. K. In "The Photosynthetic Bacteria"; Clayton, R. K., Sistrom, W. R., Eds.; Plenum Press: New York, 1978; pp 387–396.

(3) Lindsey, J. S.; Mauzerall, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4498–4500.

(4) Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1978–1985.

(5) Livingston, R.; Ke, C. L. *J. Am. Chem. Soc.* **1950**, *72*, 909–914. Hales, B. J.; Bolton, J. R. *Ibid.* **1952**, *94*, 3314–3320. Gouterman, M.; Holton, D. *Photochem. Photobiol.* **1977**, *25*, 8591.

(6) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407–2411.

(7) Andrews, L. J.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304–2309.

0002-7863/83/1505-6528$01.50/0