for abstraction was found to depend on the concentration of starting material,[14] and consequently it was not possible to determine the rate of hydrogen transfer by Cristol's method. As may be noted from Table I, the quantum yields for hydrogen transfer decrease substantially with deuterium substitution. The relative lifetime of the triplet states of the deuterated and nondeuterated symmetrical cyclopropenes may be estimated from the relative ratios of the Stern–Volmer slopes.

$$(\Phi_H/\tau_H)(\tau_D/\Phi_D) = k_H/k_D$$

Our work shows that the triplet lifetimes are very similar (ca. within 10%) and consequently the ratio of quantum yields provides a good indication of the magnitude of the primary deuterium isotope effect.[17] The results obtained with the symmetrical cyclopropenes indicate that the deuterium isotope effect for the γ-abstraction reaction corresponds to k_H/k_D = 23 for **1** vs. **15** and k_H/k_D = 17 for **11** vs. **17**. *The primary isotope effect found with these two systems is significantly larger than any previously reported value for hydrogen transfer to an excited state.* In contrast to the results obtained with **15** and **17**, a much smaller effect on the quantum efficiency of product formation was observed with the unsymmetrical cyclopropenes **16** and **18** (i.e., $k_H/k_D \sim 3.3:1$).

The magnitude of the primary isotope effect in a hydrogen-transfer reaction has been suggested to depend on the symmetry of the transition state and is a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred.[18] Calculations of isotope effects for simplified models of hydrogen-transfer reactions are consistent with the conclusion that the isotope effect should pass through a maximum for a symmetrical transition state.[19] Apparently, the transition state for the hydrogen-transfer reaction with cyclopropenes **15** and **17** is very nearly symmetrical and the isotope effect is near the maximum value.[20] A substantial tunnel correction is necessary to reconcile these results with absolute reaction rate theory.[19] Thus, a plausible explanation to account for the large deuterium isotope effect is that the barrier for hydrogen transfer with cyclopropenes **15** and **17** is high and thin, which is the ideal situation for tunneling.[21]

Hammond's postulate suggests that the most symmetrical transition state should occur for that case in which the heat of reaction is most nearly zero.[22] Biradical formation from the symmetrical cyclopropene involves the making and breaking of bonds with similar dissociation energies. With the 1,3-diphenyl-substituted systems, hydrogen abstraction occurs on the methyl-bearing carbon atom and therefore the heat of reaction would be expected to be considerably more exothermic. The greater exothermicity of biradical formation with the unsymmetrical cyclopropenes is in accord with the smaller kinetic isotope effect for hydrogen transfer. In fact, the values obtained ($k_H/k_D \sim 3.3$) correlate well with related results in the literature.[23,24]

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α Deprotonation of β-Lactones—an Example of a "Forbidden" β Elimination

Sir:

The stereochemistry of β eliminations has been investigated extensively for decades;[1] from the data which have thus been accumulated it clearly emerges that β eliminations of any type can only proceed if the electron-donating (β) and the electron-accepting (α) orbital adopt a syn or an anti arrangement. We term these eliminations "allowed". By contrast, the process may be considered "forbidden" if α and β are fixed in a strictly orthogonal position (Chart I). We report here that the 3-deprotonated 2-oxetanones (β-lactones) **2** are surprisingly stable and that an orthogonal orbital arrangement may be held responsible for this phenomenon.

2 was generated by deprotonation of the corresponding β-lactone (2-oxetanone)[2] (**1**) with lithium diisopropylamide in THF at −78 °C (Scheme I); at this temperature **2** remains unchanged and adds a variety of electrophiles at C-3 (Table I).[3] On warming to room temperature the expected β elimination slowly occurs and the acrylic acid anion **5** is formed in quantitative yield.[4] Apparently, the conversion of **1** into **5** represents the first E1cB elimination with an oxygen leaving group in which the carbanion intermediate can be trapped with electrophiles.[5]

The stability of **2** is surprising because β-acyloxy and β-alkoxy carbanions are very liable toward elimination if their *O*-acyl (or *O*-alkyl) moiety is part of a small ring.[6] In fact we

Chart I

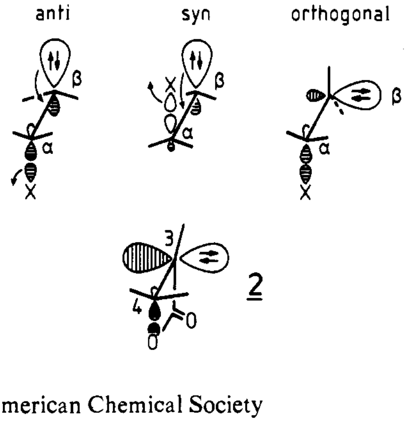
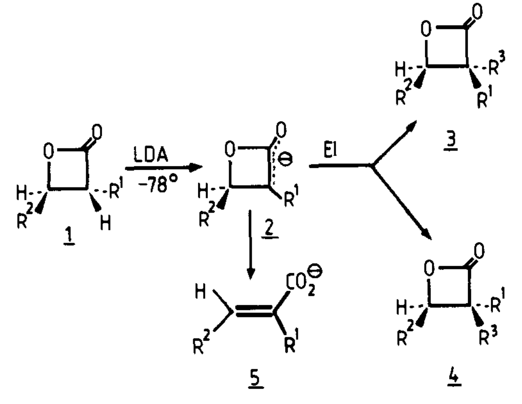


Table I. β-Lactone Derivatives **3** and Ratios of **3**:**4**

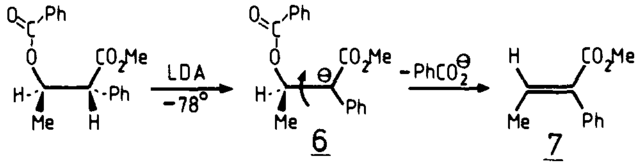
β-lactone anion	R^1	R^2	R^3 (El)	**3**	yield, %; bp (mmHg) or mp, °C	ratio of **3**:**4**[a]
2a	Ph	*t*-Bu	$-CH_3$ (CH_3I)	**3a**	99; 110-110.5	>98:2
	Ph	*t*-Bu	-Et (EtI)	**3b**	76; 81.5-82.5	>98:2
	Ph	*t*-Bu	$-CH_2C_6H_5$ ($C_6H_5CH_2Br$)	**3c**	75; 152.5-153	>98:2
	Ph	*t*-Bu	$-CH_2CO_2CH_3$ ($CH_3O_2CCH_2Br$)	**3d**	82; 68.5-69	>98:2
2b	Ph	*i*-Pr	$-CH_3$ (CH_3I)	**3e**	97; 51-51.5	>98:2
	Ph	*i*-Pr	$-CH_2CH{=}CH_2$ ($H_2C{=}CHCH_2Br$)	**3f**	93; 53-54	>98:2
	Ph	*i*-Pr	$-CO_2CH_3$ ($Cl-CO_2CH_3$)	**3g**	83; 55-55.5	>98:2
	Ph	*i*-Pr	$-CH_2C{\equiv}CH$ ($HC{\equiv}CCH_2Br$)	**3h**	98; 100-110 (0.2)	>98:2
	Ph	*i*-Pr	$C_6H_5C({=}O)-$ [$C_6H_5C({=}O)Cl$]	**3i**	78; 96-97	>98:2
2c	Ph	Et	$-CH_3$ (CH_3I)	**3j**	78; 58-59	89:11
2d	Ph	CH_3	$-CH_3$ (CH_3I)	**3k**	92; 90-100 (0.2)	90:10
2e	CH_3	*t*-Bu	$-CH_3$ (CH_3I)	**3l**	93; ~20	
	CH_3	*t*-Bu	$-CH_2C_6H_5$ ($C_6H_5CH_2Br$)	**3m**	99; 54-55	>98:2

[a] Determined by ^1H NMR.

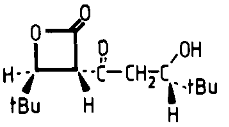
Scheme I



calculate an enthalpy[7] of −18 kcal mol^{-1} for the rearrangement of **2** → **5**. Why is **2** so amazingly stable? A most straightforward explanation lies in the assumption that, on account of the rigid geometry of **2**, the orbitals α and β are held in an orthogonal arrangement[8] (Chart I). The conformational inflexibility of the β-lactone ring, which is an indispensable presupposition in this case, is proved by the invariability of the coupling constants $J_{3,4}$(cis) and $J_{3,4}$(trans) in the ^1H NMR spectra of a wide variety of cis- and trans-3,4-disubstituted β-lactones **1**.[9] Owing to the enolate resonance, **2** can be expected to be even more rigid than **1**. We have corroborated our argumentation by preparing an open-chain analogue (**6**) of **2d** under the conditions described above. **6** is conformationally mobile and should eliminate; so it is not surprising that **7** is readily formed even at −78 °C.



2 is not only a mechanistically interesting species, it may also be of synthetic utility. Firstly, the reaction of **2** with electrophiles generates β-lactones with unusual substitution patterns (e.g., **3d**, **3g**, **3i**), which would be difficult to prepare by other routes. Secondly, owing to the planarity of **2**, R^2 at C-4 exerts a strongly stereocontrolling effect and directs the electrophilic attack at C-3 into the trans position with high selectivity. It is known that β-lactones like **3** can stereospecifically be converted into olefins[2] or—if an isopropyl or *tert*-butyl group is present at C-4—into γ-lactones[10] (2-oxolanones). **2** thus represents an equivalent of a vinyl anion (**8**) or a 3-(2-oxolanonyl) anion (**9**) with fixed stereochemistry.[11] Thirdly, experimental work



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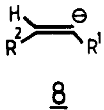

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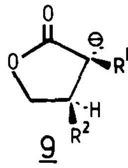

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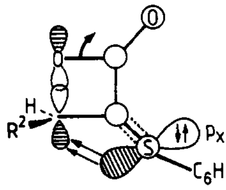
is underway in our laboratory directed to make preparative use of the functionality which has been introduced into **3** by means of El.[12]

2f (R^1 = H; R^2 = *t*-Bu) cannot be intercepted with electrophiles; in this case the totally unhindered C-3 very quickly attacks the carbonyl group of another molecule, **1f**, to form the dimer **10** (90%, mp 78-79 °C).[3]

2g (R^1 = SPh; R^2 = *i*-Pr) and **2h** (R^1 = SPh; R^2 = *t*-Bu) rearrange to **5g** and **5h** so rapidly even at −78 °C that no electrophilic attack can compete. Presumably the carbanionic



2g,h

center at C-3 in **2g**/**2h** is stabilized by a d_π-p_π interaction (dotted lines) with the S atom. At the same time, negative charge is transmitted from the filled p_x orbital of the sulfur to the emptying orbital at C-4. By means of this mediating effect of the sulfur the originally "forbidden" elimination becomes an allowed one.

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(3) All new compounds have been characterized by IR and ^1H NMR spectroscopy and give correct combustion analyses.

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(7) This enthalpy is made up by the following contributions: bond contribution,[7a] -(C═C) + (C—C) + (C—O) = +22 kcal mol^{-1}; resonance contribution, enolate resonance energy (estimd) − carboxylate resonance energy (estimd) (20 − 34) = −14 kcal mol^{-1}; contribution of ring strain,[7a] −26 kcal mol^{-1}, sum, −18 kcal mol^{-1}.[7b] (a) Adapted from Benson, S. W. "Thermochemical Kinetics", Wiley: New York, 1968. (b) The actual enthalpy should be even more negative, because the lithium cation gains in solvation energy by getting attached to a carboxylate instead of an enolate function.
(8) It might be argued that the difficulty to eliminate HX from systems like 1-halobicyclo[2.2.1]heptane, etc. is also due to an orthogonal orbital arrangement. However, in these cases the elimination leads to an unstable olefin (Bredt's rule; cf. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973,** *12*, 464), whereas in our case the "forbidden" β elimination furnishes the stable acrylic acid anion. An argumentation similar to ours, but concerning a different type of elimination, has been put forward by P. Deslongchamps in a series of excellent papers: Deslongchamps, P.; Chenevert, R.; Taillefer, R. J.; Moreau, C.; Saunders, J. K. *Can. J. Chem.* **1975,** 53, 1601. Deslongchamps, P.; Dube, S.; Lebreux, C.; Patterson, D. R.; Taillefer, R. J. *Ibid.* **1975,** *53*, 2791. Deslongchamps, P.; Taillefer, R. J. *Ibid.* **1975,** *53*, 3029. Stable 2-thietanone anión: Carter, S. D., Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* **1977,** 92.
(9) We have synthesized more than 20 pairs of 3,4-disubstituted cis–trans β-lactone isomers. In all cases, even for extreme steric congestion (e.g., *cis*-3,4-di-*tert*-butyl-, or *cis*-3-*tert*-butyl-4-mesityl (substitution), we always found that $J_{3,4}$(cis) = 6.5 Hz and $J_{3,4}$(trans) = 4.5 ± 0.5 Hz.
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(11) This is of particular interest, because 1-lithio-1-phenylalkenes are configurationally unstable in THF even at −60 °C; cf. Panek, E., Neff, B., Houng Chu, Panek, M. *J. Am. Chem. Soc.* **1975,** *97*, 3996. Similarly, direct alkylation of 3-(2-oxolanonyl) anions often proceeds unstereoselectively; cf. Grieco, P. A. *Synthesis* **1975,** 67.
(12) E.g. hydration of the triple bond in **3h,** oxidation of the double bond in **3f,** derivatization of the ester groups in **3d** and **3g**; subsequently olefins or γ-lactones may be formed according to ref 2 or 10.

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Osmochromes (Osmium Analogues of Hemochromes): Proof of Superoxide and Hydroperoxide Generation from Dioxygen and a Metalloporphyrin Lacking a Free Coordination Site

Sir:

For several years it was believed that iron(II) porphyrins, Fe(P),[1] and heme proteins are autoxidized via an inner-sphere mechanism,[2] the first step being coordination of the dioxygen molecule to the heme iron (eq 1), the second step being the attack of a second heme to the dioxygen ligand (eq 2), and the third step being nucleophilic substitution of the superoxide ion, e.g., by chloride[3] (eq 3a) or proton-assisted dissociation (eq 3b):[2c]

$$\mathrm{Fe(P)L_2} \overset{-\mathrm{L}}{\rightleftharpoons} \mathrm{Fe(P)L} \overset{\mathrm{O_2}}{\rightleftharpoons} \mathrm{Fe(P)O_2(L)} \tag{1}$$

$$\mathrm{Fe(P)O_2(L)} \xrightarrow[-2\mathrm{L}]{\mathrm{Fe(P)L}} \mathrm{(P)FeOOFe(P)} \xrightarrow[-2\mathrm{L}]{\mathrm{2Fe(P)L}} \mathrm{2(P)FeOFe(P)} \tag{2}$$

$$\mathrm{Fe(P)Cl} \xleftarrow[-\mathrm{O_2^-},\ -\mathrm{L}]{\mathrm{a.}\ +\mathrm{Cl^-}} \mathrm{Fe(P)O_2(L)} \xrightarrow[-\mathrm{HO_2\cdot}]{\mathrm{b.}\ \mathrm{H^+}} \mathrm{Fe(P)L^+} \tag{3}$$

Steps 3a or 3b should then be followed by the superoxide disproportionation reactions 4a,b or 4b in protic media:

$$\mathrm{O_2^-} + \mathrm{H^+} \xrightarrow{\mathrm{a}} \mathrm{HO_2\cdot} \xrightarrow{\mathrm{b.}\ 2\times} \mathrm{H_2O_2} + \mathrm{O_2} \tag{4}$$

If reactions 1–3 were the only possible autoxidation pathways of hemochromes Fe(P)L$_2$, one could not understand how those cytochromes are autoxidized that do not bind carbon monoxide,[4] e.g., cytochrome b_5, and thus do not offer a free coordination site. Therefore, on the basis of our experiments with osmium porphyrins, we have suggested that cytochromes can be autoxidized by an outer-sphere mechanism producing superoxide;[5] in this paper, we extend this suggestion to hemochromes as well. Equilibrium

$$\mathrm{Fe(P)L_2} + \mathrm{O_2} \underset{\mathrm{b}}{\overset{\mathrm{a}}{\rightleftharpoons}} [\mathrm{Fe(P)L_2}]^+ + \mathrm{O_2^-} \tag{5}$$

which describes this outer-sphere process may itself lie far on the left, but in protic media the successive superoxide dismutation along steps 4a,b could drive it to the right.

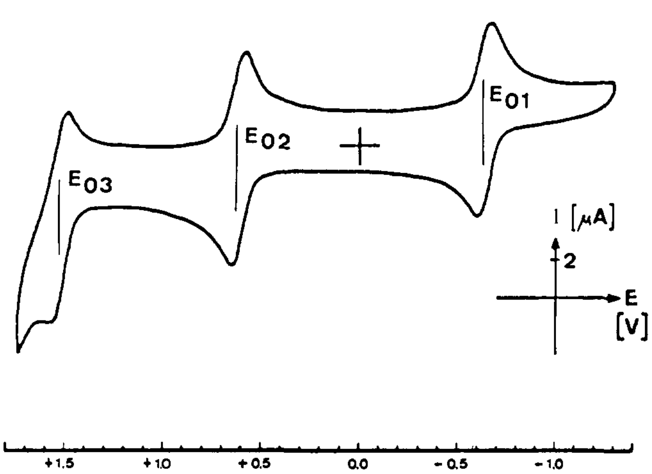

Figure 1. Cyclic voltammogram of Os(OEP)(1-Meim)$_2$ taken in CH$_2$Cl$_2$ (Beckman Pt button, scan rate, 0.1 V/s; NBu$_4$PF$_6$, 0.1 M, reference, saturated NaCl/calomel electrode): E_{O1}, Os$^{\mathrm{II}}$/Os$^{\mathrm{III}}$ step, −0.63 V; E_{O2}, Os$^{\mathrm{III}}$/Os$^{\mathrm{IV}}$ step, +0.61 V; ring oxidation, ca. +1.5 V.

With iron porphyrins,[6a,b] manganese porphyrins,[6c] or ruthenium porphyrins,[6d] the products of direct inner-sphere or outer-sphere electron transfer from the metalloporphyrin to dioxygen, i.e., O$_2^-$ and its dismutation product, H$_2$O$_2$, cannot be identified because in those complexes a free coordination site can be offered which causes superoxide dismutase[6a] or catalase activity and thus destroys any O$_2^-$ or H$_2$O$_2$ formed; moreover, H$_2$O$_2$ attacks the porphyrin carbon skeleton of hemes.[2d] Therefore, porphyrin complexes of those metals cannot serve to discriminate inner-sphere and outer-sphere electron transfer to dioxygen. Nevertheless, Castro has found the rate of the autoxidation of Fe(OEP)py$_2$ to be accelerated by a pH decrease and kinetic data to be interpretable by formation of an outer-sphere charge-transfer complex, [Fe(OEP)py$_2$·O$_2$], which is protonated.[7] The data also could fit the successive steps 5a and 4a,b. Some recent ruthenium work points also toward this direction.[6d] Fleischer has determined the oxygen uptake of a water-soluble hemochrome to be in accord with hydrogen peroxide formation, but he explains his kinetic results in favor of an inner-sphere process and could not detect the hydrogen peroxide.[6a]

In the course of our research on osmium porphyrins[2a,8,9] we have found that the "osmochromes" (osmium analogues of hemochromes[5]) are very suitable models for the investigation of hemochrome (and hence also cytochrome) autoxidation, for the following reasons. (1) Osmochromes, e.g., Os(OEP)py$_2$ (**1**)[8] or Os(OEP)(1-Meim)$_2$ (**2**)[9,10] are kinetically inert below 100 °C, i.e., stable to axial ligand exchange, e.g., carbon monoxide binding. (2) As a consequence of this, autoxidation does not occur in aprotic media. (3) Hydrogen peroxide does not attack the carbon skeleton of the osmium porphyrin at the low concentrations involved. (4) The osmochrome/osmichrome redox pair is fully reversible as evidenced by cyclic voltammetry (Figure 1),[9c,e] contrary to the substitutionally labile hemochrome/hemichrome pairs.[11] (5) The osmichrome cations are EPR silent, thus allowing a clear distinction of other radicals that might occur during the autoxidation.[12] (6) In the presence of acids, autoxidation does occur at a rate increasing with the strength of the acid present; in this autoxidation quantitative

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