10^7 cm s^{-1} at 300 K.

$$2\ Et_3Si\cdot \xrightarrow{2k_t} \text{products} \qquad (3)$$

If we make the reasonable assumption that $2k_t$ for $Et_3Si\cdot$ will be about the same as that measured for $Me_3Si\cdot$ [viz.,[5-7] $(4.0 \pm 1.5) \times 10^9$ M^{-1} s^{-1}] then ϵ_{308} is ca. 360 M^{-1} cm^{-1}.

In principle, the rate constant for reaction 2 could be measured by monitoring the formation of $Et_3Si\cdot$ following laser excitation. However, it is far more convenient to use diphenyl methanol as a probe, using the technique developed previously.[18,22] At 300 K in benzene/$Me_3COOCMe_3$ (1:2 v/v) as solvent, k_2 was found to be 6.0×10^6 M^{-1} s^{-1}.[24] For comparison, the rate constant for reaction of $Me_3CO\cdot$ with n-Bu_3SnH is 2.0×10^8 M^{-1} s^{-1},[19] and for reaction with a tertiary H in an alkane (R_3CH) is ca. 2.7×10^5 M^{-1} s^{-1},[25] at this temperature. Benzyl bromide and chloride proved well suited for the direct measurement of the absolute rate constants for halogen abstraction by $Et_3Si\cdot$, because the 316-nm band due to benzyl[27] could be monitored directly.

$$Et_3Si\cdot + PhCH_2X \rightarrow Et_3SiX + PhCH_2\cdot \qquad (4)$$

In experiments of this type the kinetic analysis is simplified and the accuracy of the rate constant is improved if the precursor radical ($Et_3Si\cdot$) is produced in a fast (formally "instantaneous") process. This was achieved by using a 2:8 (v/v) mixture of $Me_3COOCMe_3$ and Et_3SiH as solvent. At sufficiently low excitation doses[18] the formation of $PhCH_2\cdot$ followed clean first-order kinetics, and k_4 was derived from a plot of the pseudo-first-order rate constant for the buildup of the 316-nm absorption as a function of $[PhCH_2X]$. The values[24] found for k_4 at 300 K were 1.4×10^9 M^{-1} s^{-1} for $PhCH_2Br$ and $(1.4 \pm 0.4)10^7$ M^{-1} s^{-1} for $PhCH_2Cl$.

Benzil proved well suited for the direct measurement of the absolute rate constant for the addition of $Et_3Si\cdot$ to a carbonyl group, because its own absorptions are relatively weak and the structure of the adduct is known.[28]

$$Et_3Si\cdot + PhC(O)C(O)Ph \rightarrow Ph\dot{C}(OSiEt_3)C(O)Ph \qquad (5)$$

Generation of $Et_3Si\cdot$ in 1:1 (v/v) mixture of $Me_3COOCMe$ and Et_3SiH containing benzil led to transient spectra strongly resembling that of $Ph\dot{C}(OH)C(O)Ph$,[29] with maxima at 380 (strong) and 490 nm (weak). At 300 K the value of k_5 was found[24] to be 3.3×10^8 M^{-1} s^{-1}.

For organic halides which do not yield radicals that are readily detectably by optical means it is still possible to monitor the kinetics of the halogen abstraction by $Et_3Si\cdot$ by using reaction 5 as a probe, in much the same manner as diphenylmethanol is used as a probe for *tert*-butoxyl reactions.[18,19]

$$Et_3Si\cdot + RX \rightarrow Et_3SiX + R\cdot \qquad (6)$$

Thus, if benzil and an alkyl halide are both present, the buildup of the $Ph\dot{C}(OSiEt_3)C(O)Ph$ signal is modified in two ways: (i) the "plateau" signal (maximum) is reduced and (ii) the rate constant, k_{expt}, associated with the buildup increases and is now given by

$$k_{expt} = k_0 + k_5[PhC(O)C(O)Ph] + k_6\,[RX]$$

where k_0 includes any pseudo-first-order modes of decay other than reactions with the benzil or halide. The reliability of the benzil probe was checked by using benzyl chloride for which k_6 ($= k_4$) was found to be 1.8×10^7 M^{-1} s^{-1}.[24] This value is in satisfactory agreement with the value obtained by monitoring $PhCH_2\cdot$ directly (vide supra) and is, in fact, probably the more reliable because the benzil probe gives a signal of better quality. For n-pentyl bromide and chloride, values found for k_6 were 5.5×10^8 and 2.6×10^5 M^{-1} s^{-1}, respectively, at 300 K.[24] The rate constant for reaction with this chloride is in excellent agreement with a value of 2.4×10^5 M^{-1} s^{-1} at 300 K which can be calculated from the data of Cadman et al.[30] for the reaction of $Me_3Si\cdot$ with n-propyl chloride in the gas phase at high temperatures. It is worth noting that $Et_3Si\cdot$ is considerably more reactive in halogen abstractions than are trialkyltin radicals.[31] For example, with n-$Bu_3Sn\cdot$ at 298 K the rate constants for abstraciton from $PhCH_2Cl$, n-$C_5H_{11}Cl$, and n-$C_5H_{11}Br$ are 6.4×10^5, 8.5×10^2, and 1.9×10^7 M^{-1} s^{-1}, respectively.[31]

Our initial attempts to measure the rates of halogen abstraction by trialkylsilyl radicals were made by the kinetic EPR spectroscopic technique.[20] The data are less complete and less reliable but they do serve to confirm the laser results. With n-pentyl chloride the experiment were carried out in the trialkylsilane containing ca. 20% $Me_3COOCMe_3$ as solvent.

$$RMe_2Si\cdot + n\text{-}C_5H_{11}Cl \rightarrow RMe_2SiCl + n\text{-}C_5H_{11}\cdot \qquad (7)$$

$$2\ n\text{-}C_5H_{11}\cdot \rightarrow \text{nonradical products} \qquad (8)$$

For R = Me the rate constant ratio, $k_7/2k_8$, was found to be ca. 2.6×10^{-6} at 233 K, while for R = $Me_2CHCH_2CH_2$ a value of 1.1×10^{-6} was obtained at 191 K. Reasonable values for $2k_8$ are 8×10^9 M^{-1} s^{-1} in the former system and 5×10^9 M^{-1} s^{-1} in the latter, and these values yield $k_7 \sim 2.1 \times 10^4$ M^{-1} s^{-1} at 233 K and 5.5×10^3 M^{-1} s^{-1} at 191 K which seem not unreasonable at these temperatures.

Further studies on the temperature dependence of some of these reactions and on the reactivity of other silyl radicals are currently in progress. Finally, we note that the present results can be combined with the results of competitive studies reported in the literature[3c,12] to obtain absolute rate constants for other halogen abstractions by $Et_3Si\cdot$.

Acknowledgment. Thanks are due to S. Sugamori for his technical assistance.

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[22] The advantages of this technique arise from the convenient position and large extinction coefficient of the $Ph_2\dot{C}OH$ absorption.[23]

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[24] Rate constants given in this communication are reliable to better than ±15% unless otherwise indicated.

[25] Calculated from relative reactivities at 40 °C of 13.9 per hydrogen for cyclopentane and 42.4 per tertiary hydrogen for 2,3-dimethylbutane[26] and an absolute rate constant of 8.8×10^5 M^{-1} s^{-1} for cyclopentane at room temperature.[18a]

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Unusual Equilibrium between 1,4- and 1,6-Di-*tert*-butylcyclooctatetraenes

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Received January 22, 1981

We have recently had occasion to prepare 1,4-di-*tert*-butylcyclooctatetraene as a potentially interesting ligand for uranium.[1] Indeed, the corresponding uranocene did show a rotational barrier about a molecular axis that could be measured by dynamic NMR techniques.[2] The hydrocarbon itself, however, shows some unusual features as regards double bond isomerism. The hydrocarbon as prepared by oxidation of the corresponding dianion with iodine consists of an equilibrium mixture of the two double bond isomers, 1,6-di-*tert*-butylcyclooctatetraene (**1**) and the 1,4 isomer (**2**), as

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† NSF Postdoctoral Fellow, 1980.

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[2] Luke, W. D.; Streitwieser, A., Jr., *J. Am. Chem. Soc.*, in press.

Table I. Forward Rates and Equilibrium Constants for $1 \rightleftharpoons 2$

temp, °C	$10^4 k_1$, s^{-1} [a,b]	$K = [2]/[1]$ [c]
25	2.0	0.702
30	2.6	0.714
40	5.7	0.728
45	10.2	0.739
50		0.750

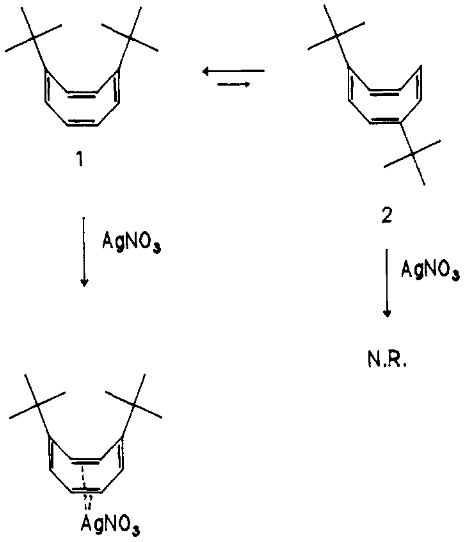
[a] Estimated error is 10%. [b] $\Delta H^{\ddagger} = 15.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -23.6$ eu. [c] $\Delta H° = 0.48$ kcal mol^{-1}, $\Delta S° = 0.92$ eu.

clearly evident in the 250-MHz spectrum. The olefinic region of **1** consists of a singlet (H 7, 8) at δ 6.05 and two broadened singlets (H 2, 3, 4, 5) at δ 5.78 and 5.63, while that of **2** consists of a singlet (H 7, 8) at δ 5.66 and a broadened AB quartet (H 5, 6, 7, 8) centered at δ 5.89 and 6.03, $J = 10.4$ Hz. This pattern is consistent with a very small coupling between H2 and H3 of **1** which are nearly orthogonal and a 10-Hz coupling between the cis olefinic H5 and H6 of **2**.

Integration gives a 1:2 ratio of **1**:**2** at 25 °C; that is, the 1,6 isomer in which both *tert*-butyl groups extend from the same side of the tub COT is actually more stable, despite the steric interactions between such *tert*-butyl groups indicated by models. Measurement of the equilibrium constant, $K = [\mathbf{2}]/[\mathbf{1}]$, by NMR integration at several temperatures gives the results summarized in Table I. Isomer **1** is more stable by $\Delta H° = 0.48$ kcal mol^{-1}, but a small entropy change of $\Delta S° = 0.92$ eu favors isomer **2**. Rotational entropy (symmetry number) and entropy of mixing (**2** exists as enantiomer pairs) contributions to the equilibrium cancel; hence, the experimental $\Delta S°$ change indicates slightly greater freedom of motion for **2**.

Why is **1**, the apparently more congested isomer, also the more stable? The only reasonable explanation is that the *tert*-butyl groups in **1** are actually positioned just at the edge of steric repulsion and intramolecular van der Waals attraction dominates. van der Waals forces are certainly important in chemistry but have rarely been implicated as a significant intramolecular effect in nonmacromolecular organic compounds.[3]

Treatment of the mixture of isomers with excess hot alcoholic silver nitrate gives a single crystalline adduct, mp 151 °C, having a satisfactory analysis.[4] The 250-MHz NMR spectra is simple, δ (CDCl$_3$) 6.31 (s, 2 H), 5.99 (br s, 2 H), 5.72 (br s, 2 H), 1.10 (s, 18 H), and is consistent only with the AgNO$_3$ complex of **1**. In **2** both faces of the tub COT are blocked by the *t*-Bu groups and adduct formation is not expected. Such an adduct would be expected to show six different olefin and two different *t*-Bu signals.



A CDCl$_3$ solution of the adduct in an NMR tube was quenched with aqueous NH$_3$ and produced signals associated with **1**. The NMR spectrum changed gradually to that of the equilibrium mixture of **1** and **2**. The reaction followed first-order kinetics, and the kinetic results at several temperatures are summarized in Table I. The activation energy is typical of other double bond isomerizations of substituted COTs,[5] but the magnitude of the entropy of activation, $\Delta S^{\ddagger} = -23.6$ eu, is unusually high for a unimolecular process. Even the isomerizations of 1,2,3-trimethyl ($\Delta S^{\ddagger} = -12$ eu) and 1,2,3,4-tetramethylcyclooctatetraenes ($\Delta S^{\ddagger} = -13.3$ eu) as reported by Paquette et al.,[6] and in which vicinal butressing effects dominate, have lower entropy demands. Evidently, in the planar [8]annulene transition state, the relatively large internal angle of the octagon (135°) results in sufficient interaction between *tert*-butyl and adjacent ring hydrogens that the *tert*-butyl motions are severely encumbered.

These results prompt additional questions concerning disubstituted cyclooctatetraenes which are currently under study in our laboratory.[7]

Acknowledgment. This work was supported in part by NSF Grant CHE 78-24084 and the Division of Nuclear Sciences, Office of Basic Energy Services, U.S. Department of Energy, under Contract W-7405-Eng-48.

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(7) After submission of this paper we learned that Professor Pacquette has independently prepared the compound and observed the transformation of **1** and **2**.

Catalysis of Ester Aminolysis by Divalent Metal Ions

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Received February 9, 1981

A number of reactions involving a variety of organic substrates possessing metal ion coordinating or -chelating sites proximate to the reactive center have been shown to be susceptible to catalysis by divalent metal ions. Such reactions include hydrolysis of nitriles,[1] esters,[2,3] amides,[4] and acetals,[5] hydration of aldehydes,[6] and formation of Schiff bases.[7] In most cases such studies, often carried out as models of enzymatic processes, have involved reactions of a hydrolytic nature; few such metal-ion-catalyzed reactions leading to more complex products have been studied, and among the exceptions,[8] the potential synthetic value lacks generality.

One class of synthetically useful reactions of considerable importance is amide bond formation; the repetitive generation of amide bonds in peptide synthesis is an obvious example of that importance. Since a variety of acyl substitution processes have been shown to be susceptible to catalysis by metal ions coordinated

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