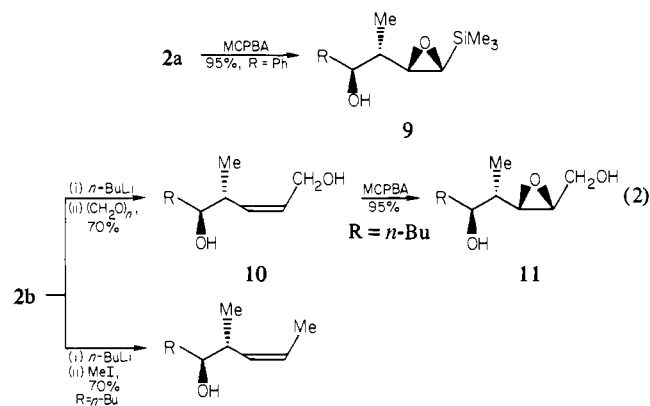


The following procedure for the synthesis of **3** is representative. In a 50-mL flask, equipped with a magnetic stirrer and maintained under a static pressure of N<sub>2</sub>, was placed dry ether (2 mL) and **1a** (1 mmol, 0.27 mL) which was prepared by the method previously described.<sup>14</sup> The solution was cooled to -78 °C and dry pyridine (2 mmol, 0.16 mL) was added. After stirring for a while, benzaldehyde (1 mmol, 0.11 mL) was added at this temperature. After 30 min, the reaction was quenched at -70 °C with MeOH (0.5 mL)—ethanolamine (2 mmol, 0.12 mL), and the mixture was allowed to warm to room temperature. The solvents were removed under vacuum, and the residual material was washed several times with hexane. The combined hexane extracts were condensed, and filtration through a column of silica gel by using petroleum ether—ether (10:1) as an eluant gave the desired isomer: 0.21 g, 90%.<sup>15</sup>

The *threo,cis*-alkenylsilanes or -stannanes (**2**) thus obtained are highly useful for the further elaboration of complex molecules. Several examples of eq 2 illustrate the flexibility inherent in these species.<sup>16</sup> We are now extending this method to the stere-



regulated synthesis of five consecutive carbon units and also the synthesis of some antibiotics.

(13) The crotyl derivative (**1**) consists of a mixture of *cis* and *trans* isomers due to the rapid allylic rearrangement.<sup>14</sup> The formation of ate complexes prevents the rearrangement, and the geometry of crotyl unit is presumably fixed to *trans*.

(14) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548.

(15) <sup>1</sup>H NMR data of the product and its isomers in Table I are as follows. Chemical shifts, not important in the structure determination, are omitted. **3** (*threo*, *Z*), (CCl<sub>4</sub>) δ 0.08 (s, 9 H), 0.76 (d, *J* = 6 Hz, 3 H, Me), 4.20 (d, *J* = 8 Hz, 1 H, CHO), 5.56 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **3** (*erythro*, *Z*) δ -0.02 (s, 9 H), 0.90 (d, *J* = 6 Hz, 3 H, Me), 4.42 (d, *J* = 6 Hz, 1 H, CHO), 5.32 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **3** (*E*, *erythro* or *threo* is not obvious) δ -0.06 (s, 9 H), 0.90 (d, *J* = 6 Hz, 3 H, Me), 4.42 (br d, 1 H, CHO), 5.50 (d, *J* = 20 Hz, 1 H, CHSi), 5.90 (d-d, *J* = 20 and 6 Hz, 1 H, =CH). These isomers were isolated from the reaction of **1a** with PcCHO in the absence of base, where considerable amounts of the byproducts were produced. **4** (*threo*, *Z*) δ 0.11 (s, 9 H), 0.75 (d, *J* = 6 Hz, 3 H, Me), 4.18 (d, *J* = 8 Hz, 1 H, CHO), 5.90 (d, *J* = 12 Hz, 1 H, CHSn), 6.26 (d-d, *J* = 12 and 10 Hz, 1 H, =CH). **5** (*threo*, *Z*) δ 0.06 (s, 9 H), 0.86 (d, *J* = 6 Hz, 3 H, Me), 3.08-3.32 (br m, 1 H, CHO), 5.51 (d, *J* = 14 Hz, 1 H, CHSi), 6.04 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **5** (*E*, *threo* or *erythro* is not obvious) δ 0.01 (s, 9 H), 0.99 (d, *J* = 6 Hz, 3 H, Me), 3.24-3.44 (br m 1 H, CHO), 5.54 (d, *J* = 20 Hz, 1 H, CHSi), 5.90 (d-d, *J* = 20 and 6 Hz, 1 H, =CH). **5** ( $\alpha$  isomer, *n*-BuCH(OH)CHSiMe<sub>2</sub>)CH=CHMe δ -0.05 (s), 1.51 (d, *J* = 6 Hz, Me), 5.44 (br s, CH=CH). **6** (*threo*, *Z*) δ 0.08 (s, 9 H), 0.91 (d, *J* = 6 Hz, Me), 3.10-3.30 (m, 1 H, CHO), 5.88 (d, *J* = 12 Hz, 1 H, CHSn), 6.26 (d-d, *J* = 12 and 10 Hz, 1 H, =CH). **7** (*threo*, *Z*) δ 0.12 (s, 9 H), 1.01 (d, *J* = 6 Hz, 3 H, Me), 3.92 (br t, 1 H, CHO), 5.59 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 16 and 7 Hz, 1 H, PhC=CH), 6.16 (d-d, *J* = 14 and 10 Hz, 1 H, CH=CSi), 6.52 (d, *J* = 16 Hz, 1 H, PhCH). **8** (*threo*, *Z*) δ 0.12 (s, 3 H), 1.00 (d, *J* = 6 Hz, 3 H, Me), 2.54 (d, *J* = 6 Hz, 2 H, CH<sub>2</sub>CO), 3.84 (quartet, *J* = 6 Hz, 1 H, CHO), 5.49 (d, *J* = 14 Hz, 1 H, CHSi), 6.17 (d-d, *J* = 14 and 10 Hz, 1 H, =CH).

(16) The epoxidation of **2a** or **10** with MCPBA proceeded with reasonable stereoselectivity, presumably owing to both the *cis* configuration and the presence of OH group. The isomer ratio was determined from the <sup>1</sup>H NMR spectra of the reaction mixture; **9**/its isomer = 85/15, being obtained from the area ratio of δ 4.53 (d, *J* = 7 Hz)/δ 4.29 (d, *J* = 8 Hz); **11**/its isomer = 88/12, from δ 4.62 (d, *J* = 7 Hz)/δ 4.36 (d, *J* = 9 Hz). See also: Johnson, M. R.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4347.

## Absolute Rate Constants for Some Reactions Involving Triethylsilyl Radicals in Solution<sup>1</sup>

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There is growing interest in the chemistry and reactivity of trialkylsilyl radicals in solution,<sup>2,3</sup> but the absolute rate constants for very few of their reactions have been measured.<sup>4</sup> Among the more interesting and important reactions of these radicals are halogen abstractions from organic halides<sup>2,3a,c,e,12-15</sup> and additions to various types of multiple bond,<sup>2,3d,f,9,14,16,17</sup> but there are no reliable rate constants for such processes. In this communication we report a kinetic study of the formation of triethylsilyl by reaction of *tert*-butoxyl radicals with triethylsilane and decay of triethylsilyl by its reaction with some organic halides and benzil. The experiments were carried out using laser flash photolysis techniques<sup>18,19</sup> supplemented by kinetic EPR spectroscopy.



Reaction 1 can be regarded as a virtually instantaneous process.<sup>18</sup> The transient absorption due to *tert*-butoxyl<sup>21</sup> are too weak to be convenient for kinetic studies. The same tends to be true of triethylsilyl which shows weak absorptions below 340 nm. However, in isooctane and triethylsilane as solvents the Et<sub>3</sub>Si· were shown to decay with second-order kinetics with  $2k_t/\epsilon_{308} = 1.1 \times$

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<sup>‡</sup> N.R.C.C. Research Associate, 1978-1979.

(1) Issued as N.R.C.C. No. 19377.

(2) For a concise review, see: Sakurai, H. *Free Radicals* **1973**, *2*, 741-808.

(3) For some interesting recent work, see, e.g.: (a) Jung, I. N.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 946. (b) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369. (c) Aloni, R.; Rajbenbach, L. A.; Horowitz, A. *Int. J. Chem. Kinet.* **1979**, *11*, 899. (d) Chen, K. S.; Foster, T.; Wan, J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1288. (e) Billingham, N. C.; Jackson, R. A.; Malek, F. *J. Chem. Soc. Perkin Trans. 1* **1979**, 1137. (f) Alberti, A.; Hudson, A.; Pedulli, G. F.; Zanirato, P. *J. Organomet. Chem.* **1980**, *198*, 145.

(4) Those known to us include only the following reactions, none of which are really suitable for competitive studies which would yield additional rate constant:  $2\text{Me}_3\text{Si}\cdot \rightarrow \text{products}$ ;  ${}^3\text{S Me}_3\text{Si}\cdot + \text{C}_2\text{H}_4 \rightarrow \text{Me}_3\text{SiCH}_2\text{CH}_2\cdot$ ;  ${}^9,10 \text{ Me}_3\text{Si}\cdot + (\text{Me}_3\text{Si})_2\text{Hg} \rightarrow \text{Me}_3\text{SiSiMe}_3 + \text{Me}_3\text{Si}\cdot + \text{Hg}$ ;  ${}^{11} \text{ Me}_3\text{Si}\cdot + (\text{Me}_3\text{Si})_2\text{Hg} \rightarrow (\text{Me}_3\text{Si})_2\text{Hg} + \text{Me}_3\text{Si}\cdot$ .

(5) Frangopol, P. T.; Ingold, K. U. *J. Am. Chem. Soc.* **1970**, *25*, C9.

(6) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 492.

(7) Gasper, P. P.; Haizlip, A. D.; Choo, K. Y. *J. Am. Chem. Soc.* **1972**, *94*, 9032.

(8) This reaction yields both combination and disproportionation products. See: Koob, R. D.; Tokach, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 376. Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. *Ibid.* **1980**, *102*, 377. Gammie, L.; Safarik, I.; Strausz, O. P.; Roberge, R.; Sandorfy, C. *Ibid.* **1980**, *102*, 378.

(9) Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 1284.

(10) It should be noted that the initial Me<sub>3</sub>Si· concentrations and the times for decay appear to be remarkably similar in the absence of ethylene<sup>7</sup> and in its presence<sup>9</sup>.

(11) Lehnig, M.; Werner, F.; Neumann, W. P. *J. Organomet. Chem.* **1975**, *97*, 375.

(12) Nagai, Y.; Yamazaki, K.; Shiojima, I.; Kobori, N.; Hayashi, M. *J. Organomet. Chem.* **1967**, *9*, P21.

(13) Hudson, A.; Jackson, R. A. *Chem. Commun.* **1969**, 1323.

(14) Bowles, A. J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc. B* **1971**, 1947.

(15) Sommer, L. H.; Ulland, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 3803. (16) Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933.

(17) Schroeder, B.; Neumann, W. P.; Hillgärtner, H. *Chem. Ber.* **1974**, *107*, 3494.

(18) (a) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520. (b) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49.

(19) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399.

(20) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193, 317.

(21) In the photodecomposition of Me<sub>3</sub>COOCMe<sub>3</sub> (monitored at λ > 305 nm) weak signals peaking at 320 nm are observed.

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



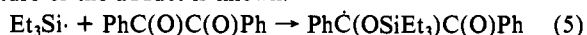
If we make the reasonable assumption that  $2k_1$  for  $\text{Et}_3\text{Si}\cdot$  will be about the same as that measured for  $\text{Me}_3\text{Si}\cdot$  [viz.,<sup>5-7</sup>  $(4.0 \pm 1.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ] then  $\epsilon_{308}$  is ca.  $360 \text{ M}^{-1} \text{ cm}^{-1}$ .

In principle, the rate constant for reaction 2 could be measured by monitoring the formation of  $\text{Et}_3\text{Si}\cdot$  following laser excitation. However, it is far more convenient to use diphenyl methanol as a probe, using the technique developed previously.<sup>18,22</sup> At 300 K in benzene/ $\text{Me}_3\text{COOCMe}_3$  (1:2 v/v) as solvent,  $k_2$  was found to be  $6.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>24</sup> For comparison, the rate constant for reaction of  $\text{Me}_3\text{CO}\cdot$  with  $n\text{-Bu}_3\text{SnH}$  is  $2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>19</sup> and for reaction with a tertiary H in an alkane ( $\text{R}_3\text{CH}$ ) is ca.  $2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>25</sup> at this temperature. Benzyl bromide and chloride proved well suited for the direct measurement of the absolute rate constants for halogen abstraction by  $\text{Et}_3\text{Si}\cdot$ , because the 316-nm band due to benzyl<sup>27</sup> could be monitored directly.



In experiments of this type the kinetic analysis is simplified and the accuracy of the rate constant is improved if the precursor radical ( $\text{Et}_3\text{Si}\cdot$ ) is produced in a fast (formally "instantaneous") process. This was achieved by using a 2:8 (v/v) mixture of  $\text{Me}_3\text{COOCMe}_3$  and  $\text{Et}_3\text{SiH}$  as solvent. At sufficiently low excitation doses<sup>18</sup> the formation of  $\text{PhCH}_2\cdot$  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  $[\text{PhCH}_2\text{X}]$ . The values<sup>24</sup> found for  $k_4$  at 300 K were  $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{PhCH}_2\text{Br}$  and  $(1.4 \pm 0.4)10^7 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{PhCH}_2\text{Cl}$ .

Benzil proved well suited for the direct measurement of the absolute rate constant for the addition of  $\text{Et}_3\text{Si}\cdot$  to a carbonyl group, because its own absorptions are relatively weak and the structure of the adduct is known.<sup>28</sup>



Generation of  $\text{Et}_3\text{Si}\cdot$  in 1:1 (v/v) mixture of  $\text{Me}_3\text{COOCMe}$  and  $\text{Et}_3\text{SiH}$  containing benzil led to transient spectra strongly resembling that of  $\text{PhC(OH)C(O)Ph}$ ,<sup>29</sup> with maxima at 380 (strong) and 490 nm (weak). At 300 K the value of  $k_5$  was found<sup>24</sup> to be  $3.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

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  $\text{Et}_3\text{Si}\cdot$  by using reaction 5 as a probe, in much the same manner as diphenylmethanol is used as a probe for *tert*-butoxyl reactions.<sup>18,19</sup>



Thus, if benzil and an alkyl halide are both present, the buildup of the  $\text{PhC(OSiEt}_3\text{)C(O)Ph}$  signal is modified in two ways: (i) the "plateau" signal (maximum) is reduced and (ii) the rate constant,  $k_{\text{expt}}$ , associated with the buildup increases and is now given by

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

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  $1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>24</sup> This value is in

(22) The advantages of this technique arise from the convenient position and large extinction coefficient of the  $\text{Ph}_2\text{COH}$  absorption.<sup>23</sup>

(23) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. Kiryukhin, Y. I.; Sinitsyna, Z. A.; Bagdasar'yan, Kh. S. *High Energy Chem.* **1979**, *13*, 432.

(24) Rate constants given in this communication are reliable to better than  $\pm 15\%$  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<sup>26</sup> and an absolute rate constant of  $8.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for cyclopentane at room temperature.<sup>18a</sup>

(26) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877.

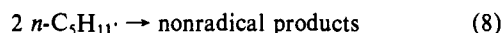
(27) Joschek, H. I.; Grossweiner, L. I. *J. Am. Chem. Soc.* **1966**, *88*, 3261.

(28) Alberti, A.; Hudson, A. *Chem. Phys. Lett.* **1977**, *48*, 331.

(29) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

satisfactory agreement with the value obtained by monitoring  $\text{PhCH}_2\cdot$  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  $5.5 \times 10^8$  and  $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at 300 K.<sup>24</sup> The rate constant for reaction with this chloride is in excellent agreement with a value of  $2.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 300 K which can be calculated from the data of Cadman et al.<sup>30</sup> for the reaction of  $\text{Me}_3\text{Si}\cdot$  with *n*-propyl chloride in the gas phase at high temperatures. It is worth noting that  $\text{Et}_3\text{Si}\cdot$  is considerably more reactive in halogen abstractions than are trialkyltin radicals.<sup>31</sup> For example, with *n*- $\text{Bu}_3\text{Sn}\cdot$  at 298 K the rate constants for abstraction from  $\text{PhCH}_2\text{Cl}$ , *n*- $\text{C}_5\text{H}_{11}\text{Cl}$ , and *n*- $\text{C}_5\text{H}_{11}\text{Br}$  are  $6.4 \times 10^5$ ,  $8.5 \times 10^2$ , and  $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>31</sup>

Our initial attempts to measure the rates of halogen abstraction by trialkylsilyl radicals were made by the kinetic EPR spectroscopic technique.<sup>20</sup> 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%  $\text{Me}_3\text{COOCMe}_3$  as solvent.



For  $\text{R} = \text{Me}$  the rate constant ratio,  $k_7/2k_8$ , was found to be ca.  $2.6 \times 10^{-6}$  at 233 K, while for  $\text{R} = \text{Me}_2\text{CHCH}_2\text{CH}_2$  a value of  $1.1 \times 10^{-6}$  was obtained at 191 K. Reasonable values for  $2k_8$  are  $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in the former system and  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in the latter, and these values yield  $k_7 \sim 2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 233 K and  $5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  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<sup>3c,12</sup> to obtain absolute rate constants for other halogen abstractions by  $\text{Et}_3\text{Si}\cdot$ .

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

(30) Cadman, P.; Tilsley, G. M.; Trotman-Dickenson, A. F. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 914.

(31) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

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

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We have recently had occasion to prepare 1,4-di-*tert*-butylcyclooctatetraene as a potentially interesting ligand for uranium.<sup>1</sup> Indeed, the corresponding uranocene did show a rotational barrier about a molecular axis that could be measured by dynamic NMR techniques.<sup>2</sup> 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

\* NSF Postdoctoral Fellow, 1980.

(1) Miller, M. J.; Lyttle, M. H.; Streitwieser, A., Jr., *J. Org. Chem.*, in press.

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