

Table I. Crystallographic Details for (+)-17

formula	C ₂₉ H ₄₀ O ₂ Si
M _r	448.73
space group	P2 ₁ -C ₂ ²
a, Å	6.792 (2)
b, Å	18.599 (4)
c, Å	10.794 (2)
β, deg	94.97 (2)
V, Å ³	1358
Z	2
density (calcd), g/cm ³	1.097
radiation	Mo Kα (λ(Kα ₁) = 0.70926 Å, with graphite monochromator)
linear abs coeff, cm ⁻¹	1.03
temp	20 (1) °C
2θ limits	4° ≤ 2θ ≤ 55°
scan speed	1.0-24.0°/min
background time/scan time	0.5 s
scan range	1.0° below Kα ₁ to 1.0° above Kα ₂
data collected	+h, +k, ±l
unique data	2485
unique data with F _o ² > 2σ(F _o ²)	1734
final number of variables	212
R(F)	0.064
F _w (F)	0.055
error in observation of unit weight, e	1.94

CHCl₃; IR (neat, cm⁻¹) 1678, 1673; ¹H NMR (CDCl₃) δ 8.2-8.0 (m, 2 H), 7.7-7.0 (m, 13 H), 3.65 (d, J = 7.5 Hz, 1 H), 2.04 (d, J = 7.5 Hz, 1 H), -0.14 (s, 9 H). This material was not further purified.

Haller-Bauer Cleavage of (-)-18. A mixture of **18** (0.075 g, 0.20 mmol), [α]_D^{22.5} -84°, sodium amide (0.050 g, 1.3 mmol), and dry benzene (4 mL) was heated at reflux for 20 h. Following the prescribed workup, there was isolated 0.011 g (20%) of **13**, [α]_D^{22.5} -96° (c 1.06, CHCl₃); the ¹H NMR spectrum was identical with those obtained with the samples of this silane prepared earlier.

1-Menthyl (+)-1-(S)-3-(S)-2,2-Diphenyl-3-(trimethylsilyl)cyclopropanecarboxylate (17). A mixture of **16** (0.092 g, 0.30 mmol), [α]_D^{22.5} +285, and thionyl chloride (0.9 g, 7.6 mmol) was heated at reflux for 2 h and the excess thionyl chloride was removed in vacuo. The residual acid chloride was taken up in dry ether (6 mL) and added to a solution of *l*-menthol (0.076 g, 0.49 mmol) in the same solvent (7 mL). The reaction mixture was heated at reflux for 1.5 h, cooled, washed with water (10 mL), dried, and evaporated. MPLC on silica gel (elution with 8% ethyl acetate in petroleum ether) and recrystallization from methanol furnished **17** (0.074 g, 55%): mp 139-140 °C; [α]_D^{22.5} +166° (c 0.95, CHCl₃); IR (KBr, cm⁻¹) 1729; ¹H NMR (CDCl₃) δ 7.5-6.8 (m, 10 H), 2.56 (d, J = 7.5 Hz, 1 H), 1.94-0.54 (series of m, 20 H), -0.16 (s, 9 H).

X-ray Crystal Structure Analysis of 17. Suitable crystals were grown from methanol and are clear, colorless, elongated rods. Preliminary film work indicated the systematic absences OkO with k = 2n+1, consistent with space groups P2₁ or P2₁/m. Because of the known chiral nature of

the molecule, P2₁ was chosen as the correct space group. The crystal used for data collection was cut from a long rod and was approximately 0.06 × 0.39 × 0.62 mm³ in size. The lattice parameters a = 6.792 (2) Å, b = 18.599 (4) Å, c = 10.794 (2) Å and β = 94.97 (2)° were determined at 20 °C from a least-squares fit of diffractometer setting angles for 15 reflections in the 2θ range 15°-21°.

Intensity data were collected by the θ-2θ scan technique on a Syntex P1 diffractometer using graphite monochromated Mo Kα radiation. Crystallographic details appear in Table I. Of the 2485 unique reflections measured, 1734 have F_o² > 2σ(F_o²) and were used in the full-matrix least-squares refinements based on F_o.³⁹

The structure was solved with MULTAN 80; twenty non-hydrogen atoms were easily located on the E-map. The remainder of the molecule was elucidated using standard structure factor and Fourier techniques. Isotropic refinement of the model with phenyl rings treated as rigid groups (C-O v 1.395 Å) converged to an R index of 0.108. After a cycle of anisotropic refinement, hydrogen atoms appeared on difference electron density maps and were added as fixed contributions to the structure factors with C-H = 0.95 Å and B_H = B_{C(iso)} + 1.0 Å². The two cyclopropyl ring hydrogens were allowed to refine. The final refinement cycle with anisotropic thermal parameters for the non-hydrogen atoms, isotropic rigid body refinement for both phenyl rings, and isotropic refinement for the cyclopropyl ring hydrogens yielded an R index of 0.064 and an R_w index of 0.055 using 1734 measurements and 212 variables. The final difference electron density map was featureless with a maximum peak height of 0.53 e Å⁻³.

Acknowledgment. This investigation was made possible by the financial support of the National Science Foundation. The mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by NSF Grant CHE-7910019) with the help of C. R. Weisenberg. The ORTEP drawings and some of the final X-ray calculations were obtained with the help of Dennis Kountz. The authors are particularly indebted to Professor Harry Walborsky for making available a generous sample of (-)-(R)-6.

Registry No. (±)-1, 88082-47-7; (±)-2, 88035-72-7; (-)-(R)-3, 88082-48-8; (-)-R-3-*l*-cinchonidine, 88082-53-5; (-)-(R)-3 methyl ester, 88035-81-8; (-)-(R)-4, 88035-73-8; (-)-(R)-5, 88035-74-9; (-)-(R)-6, 4542-82-9; (±)-9, 88056-68-2; (-)-(R)-10, 88082-49-9; (-)-(R)-11, 88035-75-0; (+)-(R)-12, 88035-76-1; **12**-ol, 88035-82-9; (-)-(R)-13, 88035-77-2; (±)-14, 88082-50-2; (±)-15, 88035-78-3; (±)-15 methyl ester, 88035-83-0; (+)-16, 88082-51-3; (-)-16, 88082-52-4; (+)-17, 88035-79-4; (-)-18, 88035-80-7; Me₃SiCl, 75-77-4.

Supplementary Material Available: Stereodrawing of the unit cell (Figure 2) and tables of bond lengths and angles, least-squares planes, torsion angles, final positional and thermal parameters, and observed and calculated structure factors (Tables II-VIII) for (+)-17 (15 pages). Ordering information is given on any current masthead page.

(39) Sheldrick, G. M. "SHELX-76. Program for Crystal Structure Determination"; University Chemical Laboratory: Cambridge, England, 1976.

Steric Effects of Bridgehead Carbons Which Are α to Carbonyls

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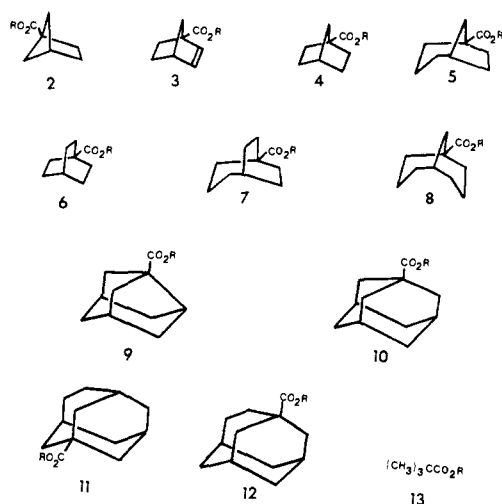
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Abstract: The rates of alkaline hydrolysis of bi- and tricyclic bridgehead substituted esters varied inversely with the size of the bridge. Enthalpy and entropy of activation were found to be related to the flexibility of the systems. The kinetic results were compared with thermodynamic data and also with recent force-field calculations. It is suggested that base-catalyzed ester hydrolysis can be used to determine the effective size of alkyl substituents.

The first fairly successful evaluation of steric effects and their separation from electronic effects was proposed by Taft, using

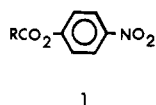
acid- and base-catalyzed hydrolysis of esters and acid-catalyzed esterification of carboxylic acids.^{1,2} Although the literature is

Chart I



replete with studies of the effects of acyclic substituents on these reactions,^{1,2} there were no comparable studies with bi- and tricyclic substituents.

In an earlier paper, we reported for the first time the steric effects of bi- and tricyclic groups on ester hydrolysis, namely the alkaline hydrolyses of a series of α -substituted-*p*-nitrophenyl carboxylates (1).³ Of particular interest was the observation that



the rigid "tied back" systems, compounds where R = 1-adamantyl or 1-bicyclo[2.2.2]octyl, appeared to have more F strain than where R = *tert*-butyl. Our results were later corroborated experimentally by Dubois and co-workers, who measured (a) the kinetics of rotation of *tert*-butyl- and 1-adamantyl-substituted groups⁴ and (b) the esterification of the relevant acids.⁵

In this work we have extended our study to a variety of bi- and tricyclic bridgehead 3,4,5-trimethoxyphenyl esters (2–12, R = 3,4,5-C₆H₂(OCH₃)₃) in order to determine the effect of bridgehead geometry upon the rate of a reaction which is minimally sensitive to polar effects.^{6,7,8}

In recent years Taft's steric parameter E_s has come under closer scrutiny. Charton has claimed that the E_s scale is faulty and that E_s is dependent solely on the van der Waals radius of the substituent.⁹ More recently, however, Dubois and co-workers have revised the Taft scale and have shown that, for very highly hindered alkyl groups, Charton's assumption is incorrect and that there is an actual leveling off and inversion of steric effect due to the specific conformation adopted by these groups.¹⁰

(1) Unger, S. H.; Hansch, C. In "Progress in Physical Organic Chemistry"; Taft, R. W., Ed.; John Wiley and Sons: New York, 1976; Vol. 12, pp 91–118 and references cited therein.

(2) Förster, H.; Vogtle, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 429 and references cited therein.

(3) Kristol, D. S.; Parker, R. C.; Perlmutter, H. D.; Chen, K.-C. H.; Hawes, D. H.; Wahl, G. H., Jr. *J. Org. Chem.* **1976**, *41*, 3205.

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(5) Panaye, A.; MacPhee, J. A.; Dubois, J.-E. *Tetrahedron Lett.* **1980**, *21*, 3485.

(6) Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552, 3691.

(7) The 3,4,5-trimethoxyphenyl esters were chosen instead of the previously employed *p*-nitro-substituted ones in an attempt to obtain a greater selectivity and thus a greater spread in rates. The rate ratios, however, did not change as much as we had hoped.

(8) Rüchardt has recently measured the rates of thermal decomposition of a series of bi- and tricyclic peresters in which he observed a trend that was more consistent with polar than with steric effects: Rüchardt, C.; Golzke, V.; Rang, G. *Chem. Ber.* **1981**, *114*, 2769.

(9) Charton, M. *J. Am. Chem. Soc.* **1969**, *91*, 615.

(10) Panaye, A.; MacPhee, J. A.; Dubois, J.-E. *Tetrahedron Lett.* **1978**, 3297. MacPhee, J. A.; Panaye, A.; Dubois, J.-E. *Tetrahedron* **1978**, *34*, 3553. Panaye, A.; MacPhee, J. A.; Dubois, J.-E. *Tetrahedron* **1980**, *36*, 759. Dubois, J.-E.; MacPhee, J. A.; Panaye, A. *Tetrahedron* **1980**, *36*, 919.

Table I. Hydrolysis of 3,4,5-Trimethoxyphenyl Carboxylates^a in 1:1 *tert*-Butyl Alcohol/0.05 M Aqueous Buffer, pH 12.5—Bicyclic Series

compd	k^b	k_{rel}^c	ΔH^\ddagger^d	ΔS^\ddagger^e	mp, °C
2	$(2.90 \pm 0.15) \times 10^{-2}$	34	12.5	-23.0	91.5–92.0
	$(6.07 \pm 0.07) \times 10^{-2}$				
	$(1.22 \pm 0.02) \times 10^{-1}$				
3	$(2.28 \pm 0.02) \times 10^{-2}$	26	12.1	-24.7	95.0–95.5
	$(4.38 \pm 0.08) \times 10^{-2}$				
	$(9.19 \pm 0.02) \times 10^{-2}$				
4	$(7.06 \pm 0.07) \times 10^{-3}$	8.2	13.1	-23.6	95.0–96.0
	$(1.50 \pm 0.03) \times 10^{-2}$				
	$(3.17 \pm 0.13) \times 10^{-2}$				
13	$(5.37 \pm 0.15) \times 10^{-3}$	6.2	13.1	-24.2	63.0–63.5
	$(1.17 \pm 0.03) \times 10^{-2}$				
	$(2.41 \pm 0.08) \times 10^{-2}$				
5	$(3.66 \pm 0.18) \times 10^{-3}$	4.3	12.6	-26.7	64.5–65.0
	$(7.21 \pm 0.01) \times 10^{-3}$				
	$(1.56 \pm 0.04) \times 10^{-2}$				
6	$(2.06 \pm 0.05) \times 10^{-3}$	2.4	13.8	-23.6	95.0–96.0
	$(4.64 \pm 0.07) \times 10^{-3}$				
	$(1.00 \pm 0.02) \times 10^{-2}$				
7	$(1.33 \pm 0.02) \times 10^{-3}$	1.5	14.5	-22.3	105.0–106.0
	$(2.82 \pm 0.05) \times 10^{-3}$				
	$(6.91 \pm 0.10) \times 10^{-3}$				
8	$(8.61 \pm 0.04) \times 10^{-4}$	1.0	13.4	-23.6	89.5–90.0
	$(1.96 \pm 0.03) \times 10^{-3}$				
	$(4.43 \pm 0.16) \times 10^{-3}$				

^a All compounds gave satisfactory C and H analyses. ^b mol/L·s at 20, 30, and 40 °C, respectively. Errors are given in standard deviations. ^c Relative to 8 at 20 °C. ^d kcal/mol. ^e cal/mol·K.

Table II. Hydrolysis of 3,4,5-Trimethoxyphenyl Carboxylates^a in 1:1 *tert*-Butyl Alcohol/0.05 M Aqueous Buffer, pH 12.5—Tricyclic Series

compd	k^b	k_{rel}^c	ΔH^\ddagger^d	ΔS^\ddagger^e	mp, °C
9	$(1.40 \pm 0.06) \times 10^{-2}$	9.8	13.2	-22.3	94.5–95.5
	$(3.27 \pm 0.17) \times 10^{-2}$				
	$(6.48 \pm 0.16) \times 10^{-2}$				
13	$(5.37 \pm 0.15) \times 10^{-3}$	3.8	13.1	-24.2	63.0–63.5
	$(1.17 \pm 0.03) \times 10^{-2}$				
	$(2.41 \pm 0.08) \times 10^{-2}$				
10	$(3.37 \pm 0.07) \times 10^{-3}$	2.4	14.0	-22.0	131.0–132.0
	$(8.08 \pm 0.14) \times 10^{-3}$				
	$(1.67 \pm 0.04) \times 10^{-2}$				
11	$(2.67 \pm 0.02) \times 10^{-3}$	1.9	14.2	-21.8	151.0–152.5
	$(5.94 \pm 0.15) \times 10^{-3}$				
	$(1.40 \pm 0.03) \times 10^{-2}$				
12	$(1.43 \pm 0.04) \times 10^{-3}$	1.0	13.4	-26.1	143.0–144.0
	$(3.34 \pm 0.16) \times 10^{-3}$				
	$(6.62 \pm 0.09) \times 10^{-3}$				

^a All compounds gave satisfactory C and H analyses. ^b mol/L·s at 20, 30, and 40 °C, respectively. Errors are given in standard deviations. ^c Relative to 12 at 20 °C. ^d kcal/mol. ^e cal/mol·K.

Charton, in his critique of Taft's work, has attempted to demonstrate that the electrical effects of alkyl groups are constant and that base- and acid-catalyzed ester hydrolyses vary solely with steric effects.⁶ This latter statement has been criticized by Dubois,¹¹ but Charton has shown that the steric effects in acid- and base-catalyzed ester hydrolyses are of different magnitudes and that basic hydrolyses require electrical effect terms as well; these latter effects do not vary with the type of alkyl group.^{12,13} Indeed, Charton concludes that the nature of the dependence of a particular reaction on alkyl group steric effect varies from one reaction to another, depending on the geometry of the transition state.¹⁴

Recently, attempts have been made to use molecular mechanics to calculate the $\Delta\Delta H_f$ of isoalkane–neoalkane,¹⁵ acid–orthoacid,¹⁶ and RMe–*t*-Bu systems¹⁷ as a measure of the energy of steric

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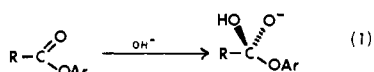
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Table III. Comparison of Beckhaus' Calculated "Front-Strain" Substituent Constant¹⁷ with our Kinetic Data

substituent	Beckhaus ξ_f^a	our log k	
<i>tert</i> -butyl	3.82	-2.72	} corr -0.70 slope -0.345
1-bicyclo[2.2.1]-heptyl	2.57	-2.59	
1-bicyclo[2.2.2]-octyl	3.49	-3.12	
1-adamantyl	4.08	-3.27	

^a Beckhaus: ξ_f vs. $\log k_{rel}$ for RCO_2H esterification (R = tertiary alkyl acyclic): corr -0.995, slope -0.835.

compression on going from carbonyl to tetrahedral intermediate in ester hydrolysis (eq 1). The steric substituent constants



calculated for 1-adamantyl, 1-bicyclo[2.2.2]octyl, and *tert*-butyl groups qualitatively conform to our earlier findings³ that the *tert*-butyl group is "smaller" than a rigid bi- and tricyclic moiety, although the quantitative comparison is far from satisfactory (vide infra).

Our kinetic results are shown in Tables I and II. The first observation is that as one increases the size of the bridges with a presumed concomitant expansion of the bond angles and flattening of the bridgehead geometry, the reactivity decreases in accord with the classical F-strain effect. However, a dissection of the rate data into their ΔH^\ddagger and ΔS^\ddagger contributions reveals some interesting characteristics. For example, the definite increase in ΔH^\ddagger as one expands from a 1-bicyclo[2.2.2]octyl (6) to a 1-bicyclo[3.2.2]nonyl (7) group can be attributed to an increase in strain energy required to proceed from an $\text{sp}^3\text{-sp}^2$ ground state to an $\text{sp}^3\text{-sp}^3$ transition state. Also, as one proceeds from a 3-noradamantyl (9) to a 1-adamantyl (10) moiety the same effect is observed. However, as one expands from a 1-bicyclo[2.2.1]heptyl (4) to a 1-bicyclo[3.2.1]octyl (5) or from a 1-adamantyl (10) to a 3-homoadamantyl (12) group one observes a decrease in ΔH^\ddagger accompanied by a very large decrease in ΔS^\ddagger which we attribute to increased flexibility in each of the larger systems. Recent force-field calculations indicate that a 1-bicyclo[3.2.1]octyl group is an unusually flexible system, much more so than a 1-bicyclo[3.2.2]nonyl group.¹⁸ First, this would explain the relative $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ in going from a 1-bicyclo[2.2.1]heptyl (4) to a 1-bicyclo[3.2.1]octyl (5) group and may explain the similar observation in the 1-adamantyl/3-homoadamantyl situation. Second, the observed large decreases in ΔH^\ddagger and ΔS^\ddagger in going from a 1-bicyclo[3.2.2]nonyl (7) to a 1-bicyclo[3.2.1]octyl (5) substituted ester serve to verify Fărcașiu's calculations.

DeTar¹⁶ and Beckhaus¹⁷ have recently used force-field calculations to predict steric substituent effects in cyclic systems. DeTar calculated the relative rate of hydrolysis of esters 4 (R = Et) and 14¹⁹ to be 4.0/1.0. We found the relative rate of hydrolysis of 4 (R = 3,4,5- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$) and 10 (R = 3,4,5- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$) to be 4.8/1.0. From DeTar's data, the relative rate of hydrolysis of 13 (R = Et) and 4 (R = Et) is 2.2/1.0. We found the relative rate of hydrolysis of 13 (R = 3,4,5- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$) and 4 (R = 3,4,5- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$) to be 1.4/1.0.

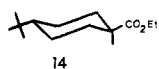


Table III shows a comparison of our results with Beckhaus's calculations where ξ_f is his steric "F-strain" parameter. Our results show an excellent correlation for the rigid systems but a less than satisfactory correlation when the *tert*-butyl group is included. Thus a *tert*-butyl group appears to be smaller than that calculated by

(17) Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 593.

(18) Fărcașiu, D., private communication.

(19) We chose DeTar's 4-*tert*-butyl-1-methylcyclohexane derivative as the closest approximation to a 1-adamantyl group since he did not use a 1-adamantyl-substituted compound.

either DeTar or Beckhaus. One must be cautious in comparing flexible acyclic systems with the more rigid bi- and tricyclic ones.

As stated earlier, Dubois has experimentally determined the relative "sizes" of 1-adamantyl and *tert*-butyl groups in two ways. The first method involved use of NMR to measure the rate of rotation about the $\text{sp}^3\text{-sp}^2$ bond of 1-adamantyl- and *tert*-butyl-substituted aryl carbinols.⁴ Replacement of a *tert*-butyl group by a 1-adamantyl moiety raised the E_{act} for rotation by 4–5 kcal/mol. In work more directly related to our own, Dubois determined his steric parameter E'_s for 1-adamantyl and *tert*-butyl by examining the relative rates of esterification of the corresponding carboxylic acids.⁵ A comparison of his results with our data is shown here:

$$\text{Dubois: } E'_{s(t\text{-Bu})} - E'_{s(1\text{-Ad})} = -1.43 - (-1.64) = +0.21$$

$$\text{Our results: } E''_{s(t\text{-Bu})} - E''_{s(1\text{-Ad})} = \log(5.37 \times 10^{-3}) - \log(3.37 \times 10^{-3}) = +0.20$$

Thus, the only two reported experimental measurements of the steric differences between *tert*-butyl and 1-adamantyl agree remarkably well and differ from calculated results,^{16,17} again pointing out the limitations of applying those calculations to rate processes. This also suggests that base-catalyzed ester hydrolysis as well as esterification⁵ may serve as the basis for a scale of steric parameters.

In an attempt to model the transition state of ester hydrolysis Wilberg measured the enthalpy of hydrolysis of ketals.²⁰ In a similar fashion we prepared and hydrolyzed the ethylene ketals of methyl 1-adamantyl ketone and methyl *tert*-butyl ketone. We calculated H_r of the two ketals in their pure liquid state to be -1.896 and -0.941 kcal/mol, respectively.

The more negative ΔH for methyl 1-adamantyl ketone, 0.945 kcal/mol, is attributed to its greater relief of strain upon being transformed from an sp^3 - to an sp^2 -hybridized carbon at the site of the ketal. The ΔH^\ddagger for hydrolysis of our 1-adamantyl carboxylate is 1.1 kcal/mol more positive than that of pivalate, a reflection of the increased crowding in proceeding from sp^2 to sp^3 hybridization. Thus, from both kinetic and thermodynamic data, the 1-adamantyl group is roughly 1 kcal/mol "larger" than a *tert*-butyl group. These results are comparable to those obtained by force-field calculations: using hydrocarbons Beckhaus calculated a $\Delta\Delta H$ for 1-adamantyl vs. *tert*-butyl of 0.62 kcal/mol with the 1-adamantyl again appearing larger.¹⁷

Thus it seems that flexibility plays a more significant role in steric effects than was previously suspected. Further thermodynamic, kinetic, and theoretical studies are in progress.

Experimental Section

Preparation of 3,4,5-Trimethoxyphenyl Carboxylates (General Procedure). The various carboxylic acids were either obtained commercially, received as donated samples, or prepared by literature procedures. Pivalic and adamantane-1-carboxylic acids were obtained from Aldrich Chemical Co. The carboxylic acid precursors to esters 2, 3, 4, 5, and 6 were donated samples. Bicyclo[3.3.1]nonane-1-carboxylic acid was prepared by a sequence of reactions²¹ starting with the commercially available bicyclo[3.3.1]nonan-9-one (Aldrich Chemical Co.). Bicyclo[3.2.2]nonane-1-carboxylic acid was prepared from bicyclo[2.2.2]octane-1-carboxylic acid by the method of Rūchardt et al.²² Noradamantane-3-carboxylic acid was prepared by the method of Jones and Schleyer.²³ Homoadamantane-1-carboxylic acid and homoadamantane-3-carboxylic acid were prepared by the method of Schleyer et al.²⁴ Each carboxylic acid was reacted with 3,4,5-trimethoxyphenol and polyphosphoric ester.²⁵ The resulting esters were purified by recrystallization from either pentane or hexane. All compounds gave satisfactory IR and NMR spectra and elemental analyses.

(20) Wiberg, K. B.; Squires, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5512.

(21) Bingham, R. C.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1198 and ref 9 cited therein.

(22) Golzke, V.; Langhals, H.; Rūchardt, C. *Synthesis* **1977**, 675.

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(25) Aldridge, V.; deCarvalho, F. R. F.; El Seoud, O. A. *An. Acad. Bras. Cienc.* **1978**, *50* (4), 499.

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Kinetic Analyses. Phosphate buffer, 0.050 M, pH 12.5, was mixed with an equal volume of *tert*-butyl alcohol. Esters of approximately 1×10^{-2} M were dissolved in acetonitrile. Reactions are initiated by injecting 100 μ L of the ester solutions into a cuvette containing 3.0 mL of the butanol-phosphate buffer which had previously been brought to the desired temperature in a Perkin-Elmer Model 571 spectrophotometer. After mixing the solution of ester in butanol-phosphate buffer, the optical density at 287 nm due to the formation of 3,4,5-trimethoxyphenol was recorded on a digital printer during the course of the first 3% of the reaction. Best fit linear regressions of these straight line regions ($r \geq 0.990$) afforded the initial rates in OD/s which were then converted to mol/L-s by dividing by the extinction coefficient of 3,4,5-trimethoxyphenol in the butanol-buffer mixture, the ester concentration in the cuvette, and the calculated hydroxide ion concentration. Analyses were performed at least three times on each ester at each temperature, 20, 30, and 40 °C.

Preparation of Ethylene Ketals of 1-Adamantyl Methyl Ketone and *tert*-Butyl Methyl Ketone. Ethylene glycol and a few milligrams of *p*-toluenesulfonic acid were reacted in benzene with 1-adamantyl methyl ketone and pinacolone, respectively, by azeotropic distillation of water. The crude ethylene ketals obtained after the usual workup were purified by either fractional distillation or preparative vapor phase chromatography. Physical and spectroscopic characteristics were identical with the literature²⁶ values in the case of the ketal derived from pinacolone. The ketal derived from 1-adamantyl methyl ketone, mp 52-53 °C, evinced spectroscopic and elemental analyses consistent with its formulation.

Heats of Hydrolysis of Ethylene Ketals. The heats of hydrolyses in a 92% aqueous dioxane solution 0.001 N in HCl were measured with an

LKB 8721-4 closed bomb reaction calorimeter in combination with an LKB 8700 Precision calorimetry system. The calibration of the calorimeter was accomplished by using THAM. For this part the calorimeter vessel was filled with 60 mL of 0.102 M HCl. The reaction was carried out in a thermostat which was controlled at 25.00 ± 0.01 °C. Resistance-time measurements were obtained to give a sufficiently long post-reaction period, about 10 min after thermal equilibrium had been reached.

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Absolute Rate Constants for the Reactions of Tri-*n*-butylgermyl and Tri-*n*-butylstannyl Radicals with Carbonyl Compounds, Other Unsaturated Molecules, and Organic Halides¹

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Abstract: The absolute rate constants for the reactions of *n*-Bu₃Ge· and *n*-Bu₃Sn· radicals with a wide variety of organic compounds have been measured in solution at ca. 300 K by using laser flash photolysis techniques. For most of the substrates examined the *n*-Bu₃Ge· and *n*-Bu₃Sn· radicals were found to have essentially equal reactivity, e.g., the measured rate constants were 7.4×10^8 and 1.4×10^9 M⁻¹ s⁻¹, respectively, for duroquinone; 9.6×10^7 and 1.3×10^8 M⁻¹ s⁻¹, respectively, for benzil; 8.6×10^7 and 9.9×10^7 M⁻¹ s⁻¹, respectively, for styrene; 4.6×10^7 and 6.8×10^7 M⁻¹ s⁻¹, respectively, for 1,4-pentadiene; and 8.6×10^7 and 1.7×10^8 M⁻¹ s⁻¹, respectively, for *tert*-butyl bromide. In all their reactions, these two radicals are less reactive than triethylsilyl radicals. From literature data we are able to estimate that the inversion of triorganogermlyl radicals is somewhat slower than that for triorganosilyl radicals.

Absolute rate constants for a wide variety of reactions involving carbon-centered radicals are available,³ but the same cannot be said for radicals centered on the other atoms from group 4.

For silicon-centered radicals the most extensive (and almost the only) absolute rate data come from our own recent work. We have measured rate constants for the formation of silyl radicals by H-atom abstraction from the parent silanes,⁴⁻⁶ for the addition

of triethylsilyl radicals to carbonyl compounds^{4,7} and other classes of unsaturated compounds,⁸ and for halogen atom abstractions by triethylsilyl.^{4,9}

Considerably less information is available regarding the absolute reactivity of tin-centered radicals. Rotating sector studies, which were reported from this laboratory in 1968,^{10,11} yielded rate constants for H-atom abstraction from tri-*n*-butyltin hydride (and

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