Figure 1. C/O for methylation of lithioisobutyrophenone (0.2 M) by methyl p-toluenesulfonate (0.24 M) in dioxolane at 30 °C.

Table I. Initial Rates (mol L^{-1} s^{-1}) for C- and O-Methylation of Lithioisobutyrophenone (0.2 M) by Methyl p-Toluenesulfonate (0.24 M) in Dioxolane at 30 °C

run	salt	[salt]	$10^6 d[C]/dt^a$	$10^6 d[O]/dt^b$	C/O^a
1			1.48 ± 0.09	0.26 ± 0.02	5.69 ± 0.15
2	$LiClO_4$	0.005	1.14 ± 0.03	0.24 ± 0.03	4.67 ± 0.08
3	$LiClO_4$	0.027	1.12 ± 0.07	0.53 ± 0.08	2.10 ± 0.03
4	$LiClO_4$	0.05	1.07 ± 0.04	0.57 ± 0.03	1.88 ± 0.05
5	$LiClO_4$	0.081	1.32 ± 0.05	1.04 ± 0.09	1.27 ± 0.03
6	$LiClO_4$	0.11	1.52 ± 0.07	1.54 ± 0.08	0.99 ± 0.02
7	$LiClO_4$	0.22	2.17 ± 0.09	2.11 ± 0.11	1.03 ± 0.03
8	$LiClO_4$	0.33	2.82 ± 0.19	3.92 ± 0.31	0.72 ± 0.03
9	$LiClO_4$	0.43	4.46 ± 0.37	5.72 ± 0.56	0.78 ± 0.04
10	$LiBPh_4$	0.007	2.99 ± 0.16	1.85 ± 0.17	1.62 ± 0.17
11	$LiBPh_4$	0.10	c	c	1.42^d
12	Bu_4NOTs	0.10	c	c	0.26^d
13	Bu_4NOTs	0.20	c	c	0.42^e
14	Bu_4NClO_4	0.10	1.54 ± 0.08	0.39 ± 0.02	3.97 ± 0.02
15	Bu_4NClO_4	0.20	1.81 ± 0.12	0.82 ± 0.06	2.21 ± 0.09
16	Bu_4NClO_4	0.50	1.83 ± 0.06	1.63 ± 0.06	1.12 ± 0.02
17	Bu_4NClO_4	0.75	2.86 ± 0.04	2.55 ± 0.6	1.12 ± 0.02

^{a} Calculated by fitting data for the first 10% of the reaction to a second-order polynomial. ^{b} Calculated from $d[C]/dt$ and C/O. ^{c} Too fast to measure. ^{d} Value at 8% reaction. ^{e} Value at 60% reaction.

Table II. Initial Rates (mol L^{-1} s^{-1}) for C- and O-Methylation of Lithioisobutyrophenone by Methyl p-Toluenesulfonate (0.4 M) in Dioxolane at 30 °C

[LiE]	$10^6 d[C]/dt^a$	$10^6 d[O]/dt$	C/O^a
0.05	1.10 ± 0.04	0.31 ± 0.01	3.52 ± 0.05
0.10	1.40 ± 0.11	0.26 ± 0.02	5.49 ± 0.05
0.20	2.19 ± 0.16	0.37 ± 0.03	5.89 ± 0.26
0.40	2.51 ± 0.31	0.35 ± 0.04	7.16 ± 0.09

^{a} See footnotes a and b for Table I.

The data in Table II can be interpreted in terms of $Li_4E_4 \rightleftarrows 2Li_2E_2$. Although the tetramer is the major species (at 0.5 M^1), the dimer is expected to be substantially more reactive.[2] Runs 1–6 in Table I also show a manifestation of this equilibrium. Low concentrations of $LiClO_4$ actually retard C-methylation presumably by converting the dimer to $Li_4E_3ClO_4$, analogous to the reported interaction of Li_2E_2 with LiCl in dimethoxyethane.[1] We postulate that this mixed aggregate is the new reactant species and that it undergoes C-methylation less rapidly than the dimer. At higher [$LiClO_4$] electrophilic catalysis prevails.

Evidence for the formation of species of the type $Li_4E_{4-n}(ClO_4)_n$ is provided by NMR studies of lithium 3,5-dimethylphenolate, which is also known[3] to be tetrameric in dioxolane. The addition of such solutions to solutions of $LiClO_4$ results in substantial increases in the line width of both ^7Li and ^{35}Cl while leaving unchanged the ipso and para ^{13}C chemical shifts which are highly characteristic of the state of aggregation[3] (see Table III). These observations are thus consistent with the formation of mixed

(2) Jackman, L. M.; Lange, B. C. J. Am. Chem. Soc. 1981, 103, 4494.
(3) Jackman, L. M.; DeBrosse, C. W. J. Am. Chem. Soc. 1983, 105, 4177.

Table III. Line Widths at Half-Height ($\Delta\nu$) for ^7Li and ^{35}Cl, C(4) Spin Lattice Relaxation Times, and C(1) and C(4) ^{13}C Chemical Shifts (δ) for Mixtures of Lithium 3,5-Dimethylphenolate and $LiClO_4$ in Dioxolane at 28 °C

[LiDMP], M	[$LiClO_4$], M	$^7Li \Delta\nu$, Hz	$^{35}Cl \Delta\nu$, Hz	C(4) T_1, s	$\delta_{C(1)}$, ppm	$\delta_{C(4)}$, ppm
0.2		1.3		0.41	167.5	117.2
0.2	0.4	5.5	130	0.46	167.4	117.5
0.4	0.4	5.5	165	0.46		
	0.4	0.9	63			

aggregates in which the local environment of the phenolate oxygen atom is the same as in the pure tetramer.

At this stage it is not possible to exclude the intervention of mixed tetramers with $n > 1$ nor is it yet clear why mixed species should undergo O-methylation more readily than the pure tetramer. Possibly the mixed aggregates can more readily open at one edge or face without actually dissociating, thereby exposing the enolate oxygen to attack by the electrophile.

Are Carbenium Ions Stabilized or Destabilized by α-Silyl Substitution? The Solvolysis of 2-(Trimethylsilyl)-2-adamantyl p-Nitrobenzoate

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There is considerable current interest in silicon chemistry.[1] Surprisingly, the effect of silicon substitution on the stability of carbenium ions remains virtually unknown and poorly understood,[1] in contrast to the plethora of analogous data for alkyl substitution.[2] Such data are mechanistically interesting and important practically, because carbenium ions substituted by silyl groups in the α or β positions are believed to be intermediates when organosilicon reagents are used in synthesis.[1] The biomimetic-type cyclization that yields D-homosteroids is one example.[3] β-Silyl substituents stabilize carbenium ions, but this effect has yet to be quantitatively elucidated.[1,4] The effect of α-silyl substitution is even qualitatively unclear.[5] Older studies suggest, largely by implication, that α-silyl substituents destabilize carbenium ions even as compared to hydrogen.[5a] Recently, Stang, Schiavelli, Apeloig, et al. failed to measure the α-effect directly because $(CH_3)_3SiCH_2X$ (1, X = $OSO_2C_6H_4CH_3$-p) solvolyses by an S_N2 mechanism, so that carbenium ions are not formed.[6] Similar studies of α-silyl vinyl cations were also inconclusive.[7] We report here that tertiary esters

(1) Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, pp 541.
(2) See, for example: "Mechanism and Theory in Organic Chemistry"; Lowry, T. H., Richardson, K. S., Eds.; Harper and Row: New York, 1981; pp 351–357.
(3) Schmid, R.; Huesmann, P. L.; Johnson, W. S. J. Am. Chem. Soc. 1980, 102, 5122. Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R. Tetrahedron Lett., 1978, 2549.
(4) Lambert, J. B.; Finzel, R. B. J. Am. Chem. Soc. 1982, 104, 2020. Jarvie, A. W. P. Organomet. Chem. Rev., Sect. A 1970, 6, 153. Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. J. Am. Chem. Soc. 1971, 93, 5715.
(5) (a) Cook, M. A.; Eaborn, C.; Walton, D. R. M. J. Organomet. Chem. 1971, 29, 389. (b) Cartledge, F. K.; Jones, J. P. Tetrahedron Lett. 1971, 2193. (c) Brook, A. G.; Pannell, K. H. Can. J. Chem. 1970, 48, 3679. (d) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. J. Am. Chem. Soc. 1982, 104, 1349.
(6) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, M. R. J. Am. Chem. Soc. 1982, 104, 6852.
(7) (a) Schiavelli, M. D.; Jung, D. M.; Vaden, A. K.; Stang, P. J.; Fisk, T. E.; Morrison, D. S. J. Org. Chem. 1981, 46, 92. (b) Apeloig, Y.; Stanger, A. Ibid. 1982, 47, 1462; 1983, 48, 5413.

substituted with an α-Si(CH$_3$)$_3$ or with an α-CH$_3$ group solvolyze (k_c mechanism) at essentially the same rate. Evaluation of ground state effects by ab initio calculations suggests that *in solution an α-trimethylsilyl group is less effective in stabilizing tertiary carbenium ions than an α-methyl group, but is more stabilizing than hydrogen.*

To circumvent the problems which did not permit the study of **1** we selected the tertiary 2-adamantyl ester **2a**. Even secondary
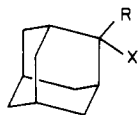
2. R = Si(CH$_3$)$_3$; 2a, X = p-O$_2$NC$_6$H$_4$COO = OPNB; 2b, X = +; 2c, X = H; 2d, X = OH
3. R = CH$_3$; 3a, X = p-O$_2$NC$_6$H$_4$COO = OPNB; 3b, X = +; 3c, X = H
4. R = C(CH$_3$)$_3$; 4a, X = p-O$_2$NC$_6$H$_4$COO = OPNB; 4b, X = +; 4c, X = H
5. R = H; 5a, X = p-O$_2$NC$_6$H$_4$COO = OPNB; 5b, X = +; 5c, X = H

adamantyl derivatives are known to solvolyse via carbenium ions by a "clean" k_c process without or with minimal solvent assistance.[8] **2a** was synthesized in 60–70% yield in a "single-pot" reaction of adamantanone with (CH$_3$)$_3$SiLi followed by the addition of p-nitrobenzoyl chloride.[9]

Solvolyses of **2a** in 80% acetone and 97% TFE follow excellent first-order kinetics. Comparison with **3a**[10] and **4a**[10] leads to the following rate ratios: In 80% acetone, $k(3a)/k(2a) = 2.18$ (at 25 °C), 2.01 (at 100 °C); $k(4a)/k(2a) = 3.6 \times 10^5$ (at 25 °C), 2.4×10^4 (at 100 °C).[11] In 97% TFE, $k(3a)/k(2a) = 0.93$ (at 25 °C).[12] Thus, *2-(trimethylsilyl)-2-adamantyl p-nitrobenzoate* (**2a**) *and 2-methyl-2-adamantyl p-nitrobenzoate* (**3a**) *solvolyze at essentially the same rate.* **2a** solvolyses ca. 10^8 times faster than the secondary adamantyl derivative **5a**,[10] and **4a** solvolyses ca. 3×10^5 times faster than **2a**. The practical constancy of $k(3a)/k(2a)$ in 80% acetone and in 97% TFE strongly supports a limiting k_c solvolysis for **2a**.[8] Significant rate acceleration of **2a** by neighboring methyl participation is unlikely as **2a** yields only 10% of the rearranged alcohol in 80% acetone.

The relative stabilities of the carbenium ions of interest (**2b–5b**) can be evaluated only if steric and electronic ground-state effects are known. The solvolysis of **4a** is accelerated by a factor of 4.5 $\times 10^5$ relatively to that of **3a** by relief of ground-state strain.[10] Is the solvolysis of **2a** also sterically accelerated? MM2 force-field calculations[13] show this not to be the case. Due to the long C–Si distance the strain in **2c** (or in **2d**) is similar to that in **3c** but much smaller than in **4c**. In contrast to **4a**, **2a** and **3a** solvolyse without significant steric acceleration.

Can electronic effects significantly change the ground-state energy of **2a** as compared to that of **3a**? Since direct experimental data are not available we rely on ab initio calculations.[14] According to eq 1 (in which alcohols model the p-nitrobenzoate esters[7b]), the α-silyl alcohols are *destabilized* relatively to the corresponding alkyl alcohols by 6–8 kcal mol^{-1}.[15]

$$R_3SiCH_2OH + R_3CCH_3 \rightarrow R_3SiCH_3 + R_3CCH_2OH \quad (1)$$

R = H $\Delta E = -7.3$ kcal mol^{-1} (MP2/6-31G*//3-21G)

R = CH$_3$ $\Delta E = -6.3$ kcal mol^{-1} (6-31G*//3-21G)

Combining these ground-state energy differences with the similar solvolysis rates of **2a** and **3a** we conclude that *in solution* an α-Si(CH$_3$)$_3$ substituent destabilizes the 2-adamantyl cation by several kilocalories per mole compared to methyl (i.e., by 6–8 kcal mol^{-1} if the gas-phase ground-state differences pertain in solution). However, in contrast to previous conclusions,[5a] an α-Si(CH$_3$)$_3$ is by ca. 12–14 kcal mol^{-1} more stabilizing than hydrogen.[16]

In the gas phase, we calculate that relatively to the corresponding hydrocarbons H$_3$SiC$^+$(CH$_3$)$_2$ is less stable than (CH$_3$)$_3$C$^+$ by 8.6 kcal mol^{-1} (at 6-31G*//3-21G). The α-silyl destabilization is even larger in secondary and primary carbenium ions; i.e., (CH$_3$)$_2$CH$^+$ and CH$_3$CH$_2$$^+$ are more stable than CH$_3$(SiH$_3$)CH$^+$ and H$_3$SiCH$_2$$^+$, respectively, by 14.3 and 18.3 kcal mol^{-1}, respectively (at MP2/6-31G*//3-21G). The (SiH$_3$)C(CH$_3$)$_{2-n}$H$_n$$^+$ cations are, however, significantly more stable than the corresponding HC(CH$_3$)$_{2-n}$H$_n$$^+$ cations. Thus, *both in solution and in the gas phase, α-silyl substitution at a carbenium ion center is destabilizing relatively to methyl but stabilizing relatively to hydrogen.* Further experimental and theoretical studies on the stabilities of other α- and β-silyl carbenium ions are in progress.

Acknowledgment. We thank the Computer Center of the Technion for generous allocation of computer time and J. Arnon for technical assistance with the calculations. This research was partially supported by the Fund for the Promotion of Research at the Technion.

(8) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.

(9) All new compounds were characterized by elemental analysis and spectroscopic methods.
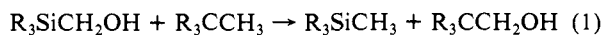
(10) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628.

(11) In 80% acetone, $k(2a) = (3.82 \pm 0.03) \times 10^{-5}$ s^{-1} (125.8 °C), $\Delta H^{\ddagger}$ = 29.4 kcal mol^{-1}, and $\Delta S^{\ddagger} = -5.0$ eu (temperature range 125–145 °C). Estimated error limits for $k(3a)/k(2a)$ are 5%.

(12) In 97% TFE $k(2a) = (7.27 \pm 0.01) \times 10^{-4}$ s^{-1} (100.2 °C), $\Delta H^{\ddagger}$ = 22.5 kcal mol^{-1}, and $\Delta S^{\ddagger} = -12.6$ eu (temperature range 75–100 °C, $r > 0.9999$). The solvolysis rate of **3a** was calculated from that of the corresponding chloride assuming a Cl/OPNB rate ratio of 9.9×10^4 (see: McManus, S. P.; Harris, J. M. *J. Org. Chem.* **1977**, *42*, 1422. Bentley, T. W.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244. Also reference 10 above).

(13) Allinger, N. L.; Yuh, Y. H. *QCPE* **1977**, *12*, 395.

(14) The GAUSSIAN 80 series of programs were used: Binkley, J. S.; Whiteside, R. M.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1980**, *13*, 406.

(15) This conclusion is supported by indirect experimental evidence. See: Peterson, P. E. *Tetrahedron Lett.* **1981**, 1295. Further discussion is given in ref 6 and 7b.

(16) The 3a/5a (or the 2a/5a) solvolysis rate ratios of 10^8 correspond to an energy difference of 11 kcal mol^{-1} at 25 °C.[8]

Conformation, Configuration, and Reactivity of Thiosulfonium Ions Derived from 1,2-Dithianes and 1,2-Dithiolanes. Stereoelectronic Effects

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Thiosulfonium ions can be prepared by alkylation of cyclic disulfides and, in this manner, S-methylated 1,2-dithianes **1–4** and dithiolanes **5–9** have been prepared as fluoroborates salts (eq 1).[1] Their conformational and configurational preferences, and
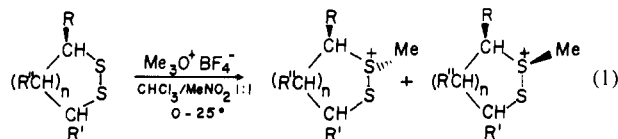
11, R = R' = R'' = H; n = 2   1
12, R = R' = Me(trans), R'' = H; n = 2   2 (100%)
13, R = R' = Me(cis), R'' = H; n = 2   3 (100%)
14, R = R' = H, R'' = (CH$_2$)$_2$(trans); n = 2   4 (100%)
15, R = R' = R'' = H; n = 1 (polymer)   5
16, R = R' = Me(trans), R'' = H; n = 1   6a (65%)   6b (35%)
17, R = R' = Me(cis), R'' = H; n = 1   7a (52%)   7b (48%)
18, R = (CH$_2$)$_4$CO$_2$Me, R' = R'' = H; n = 1   8a (26%)   8b (11%)
18, R = R'' = H, R' = (CH$_2$)$_4$CO$_2$Me; n = 1   9a (33%)   9b (30%)
                          (trans)   (cis)