a solution of hexacarbonyltungsten (1.00 g, 28 mmol) and acetonitrile (25 mL) in 50 mL of petroleum ether (100–140 °C).[35] The solution was refluxed for 44 h, then through the second neck the solvent and the unreacted acetonitrile were distilled off. To the remaining yellow-greenish residue of $(CH_3CN)_3W(CO)_3$ was added a solution of 50 mL of petroleum ether containing norbornadiene (1.15 g, 12.5 mmol). The solution was again brought to reflux for another 46 h. The liquid was decanted and the solids were extracted twice with *n*-hexane. The liquid portions were combined and evaporated to dryness on a rotary evaporator. Complex **11** was purified by passing through a silica gel column chromatograph eluted with ethyl acetate/*n*-hexane (2% v/v) and was recrystallized from *n*-hexane to form light orange crystals (140 mg, 0.36 mmol, 12%): mp 92–94 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 2 H), 1.60, 3.10 (2 t, J = 6 Hz, 2 H), 3.65, 4.00 (2 m, 2 H), 4.90, 5.50 (2 t, J = 4 Hz, 2 H); IR ($CDCl_3$) 1980 (s), 1920 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2W$: C, 45.30; H, 3.77. Found: C, 45.40; H, 3.78.

Acknowledgment. We appreciate the help from Professor K. R. Lee in the Institute of Life Science of National Tsing Hua University for recording the 2D NOESY spectra. This work was supported by the National Science Council of the Republic of China.

Supplementary Material Available: Table of final fractional coordinates of **10b** with its thermal parameters, bond angles, and bond distances; 2D NOESY spectra of **9d** and **9e**; and an orbital correlation diagram for concerted dimerization of NBD (11 pages); listing of structure factors (53 pages). Ordering information is given on any current masthead page.

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γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 2. Solvolysis of 4-(Trimethylsilyl)-2-butyl *p*-Bromobenzenesulfonates

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Abstract: The solvolysis of 4-(trimethylsilyl)-2-butyl *p*-bromobenzenesulfonate produces racemic substitution products and a minor amount of methylcyclopropane at a rate which is several-fold faster than the solvolysis of its carbon analogue; polarimetric and conductometric rates are not significantly different. Added $LiClO_4$, KOH, KOBs, and LiOBs produced normal salt effects on the polarimetric rate; b values varied from 0.2 to 130, depending on the nature of the salt and solvent. The deuterium isotope rate effects vary somewhat with solvent as follows: α-d, 1.12–1.15; β-d_3, 1.115–1.16; β-d_2, 0.975–1.07. It is concluded that the γ-silyl group promotes the solvolysis and stabilizes the intermediate carbonium ion. The "W" and "sickle" conformations of the transition states for the formation and/or reaction of the carbonium ion intermediate have approximately equal energies.

The effects of silicon substituents on carbonium ion reactions have been examined previously by several authors.[1-3] Apeloig[1c] concluded from his study of the solvolysis of 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate as compared to 2-methyl-2-adamantyl *p*-nitrobenzoate that relative to carbon, an α-silyl substituent retards sovolysis. Lambert[3] found that a β-silicon substituent greatly accelerated the solvolysis of *cis*- and *trans*-2-(trimethylsilyl)cyclohexyl trifluoroacetates. The cis isomer reacted 33 500 times faster than the unsubstituted parent but 75 times slower than the trans isomer. He suggested that electron release from the 2-Me_3Si group occurred by both inductive and hyperconjugative interactions, but later ab initio calculations by Jorgensen[4] indicated only a very small inductive effect. Fessenden[5] showed that relative to carbon, substitution by silicon at the 4-position in cyclohexyl *p*-toluenesulfonate had little or no effect on the rate of acetolysis. Fleming and Patel[6] found that treatment of γ-Me_3Si-substituted tertiary alcohols with a boron trifluoride–acetic acid complex in methylene chloride led to olefin formation via Wagner–Meerwein rearrangment and loss of the Me_3Si group. Davis was the first to report the solvolysis of γ-silyl-substituted alkyl sulfonates.[7,8] In connection with his studies of cyclopropane formation via 1,3-deoxystannylation, he solvolyzed 4-(trimethylsilyl)-2-butyl methanesulfonate. He found that the solvolysis of this compound was accelerated relative to the 2-butyl analogue in acetic acid/water solutions, even though no methylcyclopropane was found. He concluded that there was no evidence for silicon-stabilized ionic intermediates.[7] Recently we reported the study of the solvolysis of *cis*- and *trans*-3-(trimethylsilyl)-cyclohexyl *p*-bromobenzenesulfonate (brosylate or OBs). In the trans isomer we found little or no acceleration relative to the 4-*tert*-butyl analogue and large β-d_4 isotope effects on the rate. The major products were derived by direct substitution, and by a process like that reported by Fleming and Patel,[6] β-hydrogen migration followed by elimination of the Me_3Si group. In the cis compound we found a large acceleration relative to its 4-*tert*-butyl analogue with small or inverse β-d_4 isotope effects; the major products were bicyclo[3.1.0]hexane from 1,3-deoxysilylation and direct substitution with retention of configuration.[10] It was concluded that the Me_3Si group stabilizes the carbonium ion and the transition state for its formation through the "W" conformation.[11] Theoretical calculations on model compounds by Davidson[12] support this conclusion, showing that a γ-silyl-sub-

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Table I. Product Yields in Solvolysis of 4-(Trimethylsilyl)-2-butyl OBs

product[b]	solvent[a] 97T	60E	80E	90E
% alcohol	26	63	58	45
% ether	47	17	27	43
% MCP	27	20	15	12

[a] 80E and 90E are 80 and 90 vol % ethanol–20 and 10 vol % water, respectively. 97T is 97 wt % 2,2,2-trifluoroethanol and 3 wt % water. [b] Three products were identified by their characteristic ^2H chemical shifts when formed for the α-*d* reactant; the corresponding alcohol, ether, and methylcyclopropane (MCP). Errors in the yields are ±2%.

stituted carbonium ion has an energy mininum in a trans-perpendicular, cyclopropane-like conformation with a shortened C1-to-C3 distance and significant charge delocalization onto the silicon. To characterize further this previously unrecognized mode of interaction exhibited by silicon, we have examined the solvolysis of an open chain analogue, 4-(trimethylsilyl)-2-butyl brosylate, which possesses the required conformational freedom and a chiral center which allows the determination of the stereochemistry of the overall substitution reaction.

4-(Trimethylsilyl)-2-butanone was made by deprotonation of 3-(trimethylsilyl)-propanoic acid with 1 equiv of lithium hydride, followed by reaction with 1 equiv of methyllithium. 4-(Trimethylsilyl)-2-butanol and its α-*d* analogue were prepared by lithium aluminum hydride (or deuteride) reduction of the ketone. The β-d_5 ketone was produced through several exchanges with refluxing deuterium oxide containing a small amount of potassium carbonate and subsequently reduced to the β-d_5 alcohol. 3-(Trimethylsilyl)-1-propanal was prepared by a pyridinium chlorochromate oxidation of the corresponding alcohol and converted to 4-(trimethylsilyl)-2-butanol-*1,1,1*-d_3 by a Grignard reaction using methyl-d_3 iodide.[13]

(*R*)-(−)-Enriched 4-(trimethylsilyl)-2-butanol was produced by reduction of 4-(trimethylsilyl)-2-butanone with (*R*)-Alpine-hydride.[14] The relative peak heights of the methyl doublet and the Me_3Si singlet in the NMR spectrum in the presence of the chiral solvating reagent (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE)[15] indicated an enantiomeric excess (ee) of approximately 30%. Comparison with the NMR spectra of the 2-butanols of known configuration[15] indicates that the levorotatory enantiomer has the *R* configuration. The alcohols were converted to the corresponding brosylates by a modification of the Tipson procedure.[16] The alcohols and brosylates were purified by high-pressure liquid chromatography on a silica gel column using an ethyl acetate–hexane solvent mixture. ^1H (360 and 60 MHz) NMR spectra were consistent with the assigned structures. Kinetic measurements were done conductometrically[17] by using a bipolar pulse conductance apparatus[18] and polarimetrically by using a Perkin-Elmer 241 polarimeter.

The ratios of the products from the solvolysis reactions are given in Table I. The relative abundances and identity of the products were determined by analysis of reaction mixtures of the α-deuteriated compound using ^2H NMR at 55 MHz. Three products were noted: 4-(trimethylsilyl)-2-butanol, methylcyclopropane, and the corresponding ethyl or trifluoroethyl ether depending on solvent. Product ratios were determined by comparison of peak areas by using the cut and weigh technique, giving errors of about 2%. Chemical shifts, which vary slightly with solvent, are as follows in 97T (see Table I for definition of abbreviation): 4-(trimethylsilyl)-2-butanol-*2-d*, δ 3.84; 4-(trimethylsilyl)-2-butyl-*2-d* trifluoroethyl ether, δ 3.69; methylcyclopropane-*1-d*, δ 0.78. All chemical shifts are relative to external $CDCl_3$ at 7.26 ppm.

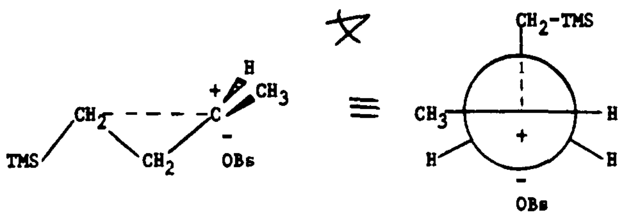

Figure 1. Silicon-promoted percaudal carbon participation.

The rate constants for the solvolysis of 4-(trimethylsilyl)-2-butyl OBs, optically active 4-(trimethylsilyl)-2-butyl OBs, 5,5-dimethyl-2-hexyl OBs, and pinacolyl OBs in several solvents at 25 °C are listed in Table II. The rate constants for the racemic compounds were determined conductometrically, with the reported rate being the average of several determinations. The rate constants for the optically active compound were the result of several determinations, measured polarimetrically with the rotation of the product mixture being virtually zero.

The isotope effects for the solvolysis of 4-(trimethylsilyl)-2-butyl OBs at 25 °C are listed in Table III. The β-d_2 effects were not measured directly but were calculated as a ratio of the β-d_5 to the β-d_3 effects.

The effects of various added salts on the polarimetric rate are given in Table IV. The plots of first-order rate constants vs. the concentration of added lithium perchlorate or potassium hydroxide are fairly linear, lithium perchlorate giving a much larger slope than potassium hydroxide which has a nearly flat response. The *b* values[19] varied as follows: 0.20, KOH, 80E; 3.8, $LiClO_4$, 80E; 7.0, KOBs, 80E; 0.40, KOH, 97T; 3.6, LiOBs, 97T; 130, $LiClO_4$, 97T.

The major product in all solvents is the result of direct substitution at the reaction center. The observation of an NMR absorption peak at approximately the region expected for methylcyclopropane-*1-d* indicates the formation of this compound via a 1,3-deoxysilylation process.

The plot of the log of the rate constants for the reacting compound vs. those for 2-adamantyl *p*-methylbenzenesulfonate (tosylate or OTs) in the same solvent, according to the "Ethanol–Trifluoroethanol" method of Raber and Harris,[20] is nearly linear with a slope (*m*) of about 0.8. Even though the 97T point falls below the correlation line for the ethanol solvents, a significant fraction of this discrepancy can be attributed to the difference in leaving groups,[21] indicating that the reaction is not nucleophilically accelerated. These data also show that the solvolysis of 4-(trimethylsilyl)-2-butyl OBs is accelerated relative to its carbon analogue, 5,5-dimethyl-2-hexyl OBs, and pinacolyl OBs. Since the yields of methylcyclopropane do not exceed 27% in any solvent, it is clear that the γ-(trimethylsilyl) substituent markedly accelerates the rate of substitution and, therefore for this limiting reaction, the rate of formation of a carbonium-ion-type intermediate. The acceleration in 97T is larger than that in ethanolic solvents and similar to that reported earlier for *cis*-3-(trimethylsilyl)-cyclohexyl OBs,[10] indicating that the γ-silyl-promoted participation established for the cyclohexyl analogue is also characteristic of the present example.

The nature of this participation is further characterized by the secondary deuterium isotope effects. The β-d_3 effects are significantly smaller (1.12 in 97T) than those for pinacolyl OBs (1.21 in 97T), indicating that the degree of orbital vacancy at the reaction center in the transition state is reduced by the action of the trimethylsilyl group. The size of the β-d_3 effects, though reduced, indicates that there is nevertheless a significant amount

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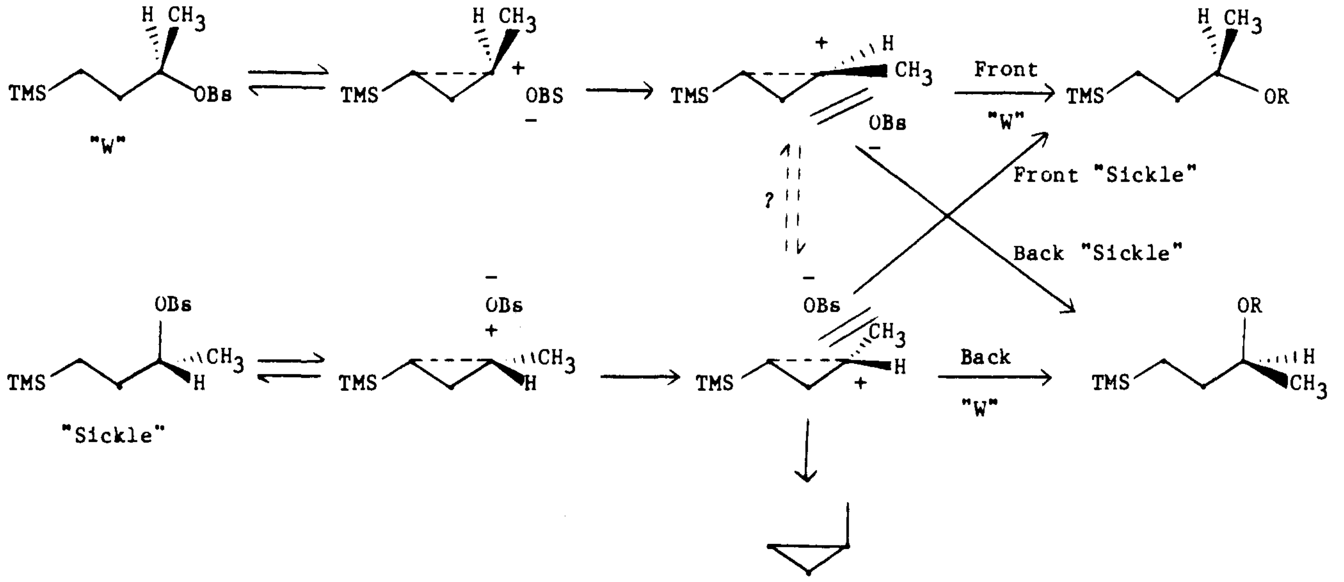

Figure 2. Mechanism for solvolysis of 4-(trimethylsilyl)-2-butyl *p*-bromobenzenebrosylate. Front or Back refers to the orientation of the incoming nucleophile with respect to the leaving group. "Sickle" or "W" refers to the conformation of the five atom chain which includes the full or partial covalent bond to the leaving or incoming group.

Table II. Rate Constants[a] for Solvolysis at 25 °C

compd	solvent[b] 97T	80E	90E
4-(trimethylsilyl)-2-butyl brosylate	84.37	4.470	1.530
5,5-dimethyl-2-hexyl brosylate	0.654	1.63	0.804
4-(trimethylsilyl)-2-butyl brosylate (opt. act)	89.2	4.24	
pinacolyl brosylate[c]	7.98	0.6357	0.190

[a] First-order rate constants in units of 10^{-5} s^{-1} for the average of several determinations done polarimetrically for the optically active compound and conductometrically for the other. [b] Solvents are as noted in Table I. [c] Fisher, R. D. Ph.D. Thesis, Indiana University, 1971.

Table III. Isotope Effects[a] for the Solvolysis of 4-(Trimethylsilyl)-2-butyl OBs at 25 °C

compd	solvent[b] 97T	80E	90E
α-*d*	1.120	1.145	1.140
β-d_5	1.090	1.185	1.230
β-d_3	1.115	1.140	1.160
β-d_2	0.975	1.040	1.060

[a] The reproducibilities of the isotope effects are between 0.005 and 0.01. [b] Solvents are as noted in Table I.

of positive charge developed at the reaction center. The fact that the β-d_2 effects are small (inverse in 97T) indicates that in the transition state, the protons on C3 are held at dihedral angles which allow for very little hyperconjugation with the reaction center. See Figure 1. This orientation is consistent with that which would be required for a cyclic transition state involving participation by carbon "percaudally"[7] through the back lobe of the carbon–silicon bonding orbital.

The α-*d* effects are also slightly smaller than those found in rate-determining ionization of secondary alkyl brosylates,[22] as expected for a transition state involving neighboring group participation.

In order to test for the occurrence of internal return, we have examined the solvolysis of 4-(trimethylsilyl)-2-butyl brosylate with both sulfonyl oxygens labeled to the extent of 90% with ^{18}O.[23-27] Unreacted sulfonate ester was recovered after partial solvolysis in 97T and 90E and analyzed by the NMR method of Van Etten,[28] making use of the $^{16}O/^{18}O$ isotope effect on the chemical shift of the α ^{13}C resonance.[29] In 90E, ester recovered after approximately two half-lives showed the presence of 20.1% ^{18}O in the ester oxygen, giving a mininum fraction of internal return ($k_e/(K_e + k_t)$) of 0.23. In 97T, ester recovered after approximately two half-lives showed the presence of 38% ^{18}O in the ester oxygen, giving a minimum fraction of internal return of 0.40. These values are larger than those for isopropyl brosylate (0.18 in trifluoroacetic acid) and smaller than those for 2-adamantyl brosylate (0.53 in 80% ethanol).[27] The ^{18}O scrambling results demonstrate the occurrence of internal return, while the absence of special salt effects and common ion effects indicates the absence of external ion pair, and external ion, return.

In contrast to the rate, product, and isotope effect results, which are typical of those associated with neighboring group participation, we find that the substitution products in this reaction, instead of having retained configuration, are racemic. In order to be consistent with the experimental evidence, the mechanism for the solvolysis of 4-(trimethylsilyl)-2-butyl OBs must involve silicon-promoted carbon participation as required by the limiting acceleration, isotope effects, and observed products. The mechanism must also involve internal return from the intimate ion pair as indicated by the ^{18}O scrambling experiments. The polarimetric rates and normal salt effects eliminate the possibility of external ion pair or external return. The rate-determining step in the Winstein ion pair solvolysis scheme[30] must be conversion of the

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Table IV. Polarimetric First-Order Rate Constants for Solvolysis of Optically Active 4-(Trimethylsilyl)-2-butyl OBs with Added Salts

	salt concentration							
salt	0.0	0.01	0.038	0.045	0.1	0.4	0.5	1.0
	Solvent: 80% Aqueous Ethanol							
$LiClO_4$	4.24	4.38			5.51	10.7	12.3	
KOH	4.24		4.52				4.81	5.23
KOBs	4.24			5.25	5.72			

	salt concentration								
salt	0.0	0.01	0.02	0.037	0.04	0.05	0.071	0.1	0.5
	Solvent: 97% Aqueous Trifluoroethanol								
$LiClO_4$	89.2	95.5	100			120		125	
KOH	89.2			97.2			99.7		102
KOBs	89.2				99.4				
LiOBs	89.2				101				

intimate ion pair to the solvent-separated ion pair ("solvent separation"). The final requirement of the mechanism is that it must account for the formation of racemic products. The mechanism we propose is shown in Figure 2. To account for racemic products, we suggest two possible explanations. First, at the solvent separated ion pair stage, the two chiral cations interconvert more rapidly than they ~~are nucleophilically attacked~~ by solvent. This would require that in the reactive ion pair intermediate the cationic centers have a much lower activation energy for rotation about the C2–C3 bond than for nucleophilic capture by solvent. Since the Me_3Si group accelerates, limiting solvolysis by a factor near 10^3, and the calculations of Davidson show a strong geometric dependence of the percaudal stabilization, this explanation seems unlikely. We prefer the second possibility, namely that silicon can stabilize carbon participation through both "W" and "endo-sickle" transition-state conformations nearly equally. The endo-sickle, hereafter and in Figure 2 denoted as simply sickle, has the brosylate group eclipsed with the C3–C4 bond (numbered as in the title compound). The exo-sickle has the trimethylsilyl group eclipsed with the C2–C3 bond and the brosylate group antiperiplanar with the C3–C4 bond.[11] Davidson's calculations, which showed that the trans-perpendicular conformation of the 3-silyl-1-propyl cation is more stable than the cis-perpendicular conformation,[12] suggest that the exo-sickle ion pair is less stable than the endo. Note that in neither the cis-perpendicular cation nor the exo-sickle ion pair is the back lobe of the C–Si bond pointed in the direction of the cationic center. In the *cis*-3-(trimethylsilyl)-cyclohexyl ester, participation can occur through the W diequatorial conformation characteristic of the initial state but not through the sickle because in that conformation the oxygen of the leaving group would occupy the position held by C6 of the ring. The same restriction does not apply to the open-chain analogue which also contrasts experimentally with the cyclic ester in giving products without stereospecificity rather than with retention. Thus, in the open-chain compound, the sickle conformation is implicated along with the W, and when the reaction scheme is referred to, it can be seen that in order to achieve nonstereospecific substitution, nucleophilic attack in the intermediate ion pair must proceed equally through both W and sickle conformations. If this is true, participation should also occur in both conformations.

Thus, the present results confirm and extend our characterization of γ-silicon-promoted carbon participation. Additional experiments to further explore the role of γ-silicon in carbonium-ion-type reactions are under way.

Experimental Section

5,5-Dimethyl-5-sila-2-hexanone. 4,4-Dimethyl-4-silapentanoic acid (3.8622 g, 1.0 equiv) was dissolved in a small amount of dry diethyl ether. This solution was added dropwise under nitrogen atmosphere to 0.2344 g (1.12 equiv) of lithium hydride suspended in 100 mL of dry diethyl ether, under anhydrous conditions at −78 °C for approximately 2–4 h. It was then allowed to warm to room temperature overnight. The reaction mixture was again cooled to −78 °C, and 40 mL of a approximately 0.7 M methyllithium solution in ether was added dropwise, with stirring. This was allowed to stir for about 4 h at −78 °C and allowed to warm to room temperature. Dry acetone (4 mL) was added to destroy any excess methyllithium. The reaction mixture was poured into 500 mL of water to hydrolyze the product. This mixture was saturated with sodium chloride, and the aqueous layer was separated from the organic layer. The aqueous layer was extracted 3 times with diethyl ether. All organic layers were combined and dried over magnesium sulfate. The solid was filtered, and the volatile organic materials were evaporated by using a rotary evaporator, leaving 5.302 g of crude product. The crude product was purified by recrystallization of the bisulfite adduct.[44] Pure 5,5-dimethyl-5-sila-2-hexanone (1.0319 g, 27%) was recovered. Typical yields ranged from 30% to 50% purified product: ^1H NMR ($CDCl_3$, 360 MHz) δ −0.007 (s, 9 H), 0.746 (t, J = 8.3 Hz, 2 H), 2.143 (s, 3 H), 2.375 (t, J = 8.3 Hz, 2 H).

1,1,1,3,3-Pentadeuterio-5,5-dimethyl-5-sila-2-hexanone. 5,5-Dimethyl-5-sila-2-hexanone (0.7109 g) was exchanged by using 99.7% perdeuteriated water (0.3% monodeuteriated and nondeuteriated water) and sodium carbonate (a catalytic amount) at reflux. 1,1,1,3,3-Pentadeuterio-5,5-dimethyl-5-sila-2-hexanone (0.3797 g, 51.6% yield, >95% pentadeuteriated by ^1H NMR) was recovered: ^1H NMR ($CDCl_3$, 60 MHz) δ −0.01 (s, 9 H), 0.7 (br s, 2 H).

5,5-Dimethyl-5-sila-2-hexanol. 5,5-Dimethyl-5-sila-2-hexanone (1.00 g, 0.00693 mol) was reduced with 0.1047 g (0.002795 mol) of lithium aluminum hydride in ether. The reaction was carried out at 0 °C and let warm to room temperature overnight. 5,5-Dimethyl-5-sila-2-hexanol (0.85 g, 83.8%) was recovered: ^1H NMR ($CDCl_3$, 360 MHz) δ −0.008 (s, 9 H), 0.49 (m, 2 H) 1.180 (d, J = 6.1 Hz, 3 H), 1.2 (m, 2 H), 1.44 (br s, 1 H), 3.698 (t of q, J_a = J_b = 6.2 Hz, 1 H).

2-Deuterio-5,5-dimethyl-5-sila-2-hexanol (1.46 g, 94.7% yield) was prepared from 1.51 g (0.01051 mol) of 5,5-dimethyl-5-sila-2-hexanone and 0.1640 g (0.003909 mol) of lithium aluminum deuteride by the same procedure as cited for the preparation of 5,5-dimethyl-5-sila-2-hexanol: ^1H NMR ($CDCl_3$, 60 MHz) δ −0.01 (s, 9 H), 0.5 (m, 2 H), 1.2 (s, 3 H), 1.5 (m, 2 H), 1.6 (s, 1 H).

1,1,1,3,3-Pentadeuterio-5,5-dimethyl-5-sila-2-hexanol (0.3620 g, 94% yield) was prepared from 0.3794 g (0.0022543 mol) of 1,1,1,3,3-pentadeuterio-5,5-dimethyl-5-sila-2-hexanone and 0.0578 g (0.001523 mol) of lithium aluminum hydride by the same procedure as cited for the preparation of 5,5-dimethyl-5-sila-2-hexanol: ^1H NMR ($CDCl_3$, 60 MHz) δ −0.01 (s, 9 H), 0.50 (br s, 2 H), 1.83 (s, 1 H), 3.65 (br s, 1 H).

4,4-Dimethyl-4-silapentanal. The oxidation of 4,4-dimethyl-4-sila-1-pentanol (2.00 g, 0.0151 mol) to 4,4-dimethyl-4-silapentanal (0.94 g, 47% yield) was accomplished by using pyridinium chlorochromate (PCC)[31] (4.95 g, 0.0230 mol): ^1H NMR ($CDCl_3$, 60 MHz) δ −0.01 (s, 9 H), 0.75 (m, 2 H), 9.65 (t, J = 2 Hz, 1 H).

Trideuteriomethyl iodide was prepared by a modified version of the preparation outlined in "Organic Syntheses".[32] Red phosphorus (3.16 g, 0.0102 mol) was placed in a receiving flask to which was attached a

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bulb-shaped modified pressure-equalizing dropping funnel fitted with a cold water condenser. Iodine crystals (38.9 g, 0.153 mol) were supported in the dropping funnel by a glass wool plug. Perdeuteriated methanol (99% D, 10.0 g, 0.278 mol) was added onto the iodine crystals and allowed to drip slowly onto the phosphorus below. When an appropriate amount of liquid collected in the receiving flask, it was immersed in a water bath and slowly warmed to reflux. The refluxing liquid, when condensed, flowed back onto the iodine crystals to continue the leaching of the iodine until all the iodine had been carried into the flask below. The reaction mixture was allowed to cool, and the dropping funnel was removed and replaced with a short-path distillation apparatus. The trideuteriated methyl iodide was distilled (bp 40–42 °C), yielding 28.10 g (69.8% yield). The ^{1}H NMR showed no peaks, as expected. Proof of purity was determined from analysis of subsequent products.

1,1,1-Trideuterio-5,5-dimethyl-5-sila-2-hexanol was formed by the reaction of (trideuteriomethyl)magnesium iodide with 4,4-dimethyl-4-silapentanal (0.94 g, 0.0072 mol). The grignard reagent was formed from 1.35 g (0.009 32 mol) of trideuteriomethyl iodide and 0.21 g (0.0086 mol) of magnesium turnings in dry diethyl ether. The crude product (1.02 g, 94% yield) was purified by using high-pressure liquid chromatography. The estimated yield was 70–80% after chromatography: ^{1}H NMR (CDCl$_3$, 360 MHz) δ −0.007 (s, 9 H), 0.50 (m, 2 H), 1.40 (m, 2 H), 3.691 (br t, J = 6.5 Hz, 1 H).

(R)-(−)-Enriched 5,5-Dimethyl-5-sila-2-hexanol. Optically active 5,5-dimethyl-5-sila-2-hexanol was prepared by reduction of 5,5-dimethyl-5-sila-2-hexanone (3.00 g, 0.0208 mol) with lithium *B*-(isopinocampheyl)-9-borobicyclo[3.3.1]nonyl hydride (44 mL of a 0.5 M solution, 0.022 mol of (*R*)-Alpine-hydride).[14] The reaction was oxidatively worked up[33] by using 21 mL of a 30% solution of hydrogen peroxide to yield a mixture of the desired alcohol, isopinocampheol, and *cis*-1,5-cyclooctanediol. The diol was partially removed by precipitation from a hexane solution. The remaining material was purified by high-pressure liquid chromatography. 5,5-Dimethyl-5-sila-2-hexanol (0.28 g, 74.9%) was recovered along with isopinocampheol and some *cis*-1,5-cyclooctanediol: specific rotation, −0.69° (589 nm sodium), −0.74° (578 nm mercury), −082° (554 nm mercury), −1.29° (436 nm mercury), −1.80° (365 nm mercury); ^{1}H NMR (CDCl$_3$, 360 MHz) δ −0.0011 (s, 9 H), 0.50 (m, 2 H), 1.178 (d, J = 6.1 Hz, 3 H), 1.41 (m, 2 H), 1.477 (br s, 1 H), 3.704 (d of t, J_a = J_b = 6.1 Hz, 1 H).

Determination of Optical Purity. The optical purity was determined by comparison of the intensities of the methyl doublet in the ^{1}H NMR using the chiral solvating reagent (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)-ethanol (TFAE).[15] By use of 300 mg of TFAE with racemic 5,5-dimethyl-5-sila-2-hexenol, the methyl doublet appeared as two doublets separated by 0.07 ppm on a 360-MHz instrument. It is assumed that peak shapes are equivalent; therefore, relative abundance was calculated from peak heights. In the racemic sample, the relative abundance was calculated as 50.1:49.9. In the optically active sample, the relative abundance was calculated as 65.8:34.2 (30.8% ee). The absolute configuration was predicted to be (*R*)-(−)-5,5-dimethyl-5-sila-2-hexanol by comparison to a spectrum of (*S*)-(+)-enriched 2-butanol taken when TFAE was used.[15] The doublet at lower field was the dominant signal and therefore corresponded to (*S*)-2-butanol. The dominant doublet in the spectrum of the optically active 5,5-dimethyl-5-sila-2-hexanol was the signal at higher field and was therefore assigned to the *R* configuration.

5,5-Dimethyl-5-sila-2-hexyl *p*-Bromobenzenesulfonate (Brosylate). 5,5-Dimethyl-5-sila-2-hexyl brosylate was prepared by a modification of the Tipson procedure.[16] Brosyl chloride (1.2013 g, 0.004 705 1 mol) was dissolved in a minimal amount of dry pyridine at 0 °C. 5,5-Dimethyl-5-sila-2-hexanol (0.6805 g 0.004 651 mol) was slowly added to this mixture. This solution was allowed to stir at 0 °C for approximately 30 min. It was then allowed to stand at approximately −10 °C for 24 h. The progress of the reaction could be estimated from the quantity of pyridinium chloride crystals formed in the flask. After the reaction was deemed complete, the liquid was decanted from the white solid into a separatory funnel. The crystals were washed 3 times with diethyl ether. The combined organic materials were neutralized by successive washings with cold 2 N sulfuric acid. The mixture was kept cold by inserting ice chips into the funnel along with the acid. When the aqueous layer used for washing was no longer basic by pH paper, the organic layer was separated and dried over magnesium sulfate. The solid was filtered through a plug of Celite/activated charcoal/Celite in a fritted funnel. The solvent was evaporated by using a rotary evaporator. The remaining material was purified by pseudorecrystallization. The liquid was dissolved in approximately 1–3 mL of ligroin, which was cooled to −78 °C. A glass formed in the flask. As much liquid was pipetted from the glass as possible. The glass was allowed to warm to room tempreature, and again 1–2 mL of ligroin were added. This procedure was repeated several times (10–20). The remaining material was once again dissolved in ligroin, dried over magnesium sulfate, and filtered, and the solvent removed by using a rotary evaporator, leaving apaproximately 0.5 g (30% yield) of a colorless liuqid: ^{1}H NMR (CDCl$_3$, 60 MHz) δ −0.01 (s, 9 H), 0.5 (m, 2 H), 1.35 (d, J = 6 Hz, 3 H), 1.65 (m, 2 H), 4.80 (q of t, J_a = J_b = 6 Hz, 1 H), 7.75 (s, 4 H).

2-Deuterio-5,5-dimethyl-5-sila-2-hexyl *p*-Bromobenzensulfonate (Brosylate). 2-Deuterio-5,5-dimethyl-5-sila-2-hexyl brosylate (approximately 0.4 g, 30% yield) was prepared from 0.5739 g (0.003 896 mol) of 2-deuterio-5,5-dimethyl-5-sila-2-hexanol and 0.9365 g (0.003 665 mol) of brosyl chloride, by the method outlined for the preparation of 5,5-dimethyl-5-sila-2-hexyl brosylate. No recrystallization was done. The compound was purified by high-pressure liquid chromatography using a Rainin HPX pump, Knauer Model 88 refractive index detector, and Rainin Dynamax$^{\text{TM}}$ 10-mm-i.d., 25 cm/L prepacked silica gel column. Typical retention times at a flow rate of 6 mL/min of a 90% hexane/10% ethyl acetate (by volume) solution are 3.5 min for brosyl chloride and 3.7 min for brosylate: ^{1}H NMR (CDCl$_3$, 60 MHz) δ −0.01 (s, 9 H), 0.50 (m, 2 H), 1.35 (br s, 3 H), 1.65 (m, 2 H), 7.75 (s, 4 H).

1,1,1,3,3-Pentadeuterio-5,5-dimethyl-5-sila-2-hexyl *p*-Bromobenzenesulfonate (Brosylate). 1,1,1,3,3-Pentadeuterio-5,5-dimethyl-5-sila-2-hexyl brosylate (approximately 0.25 g, 30% yield) was prepared from 0.3620 g (0.002 393 mol) of 1,1,1,3,3-pentadeuterio-5,5-dimethyl-5-sila-2-hexanol and 0.5400 g (0.002 113 mol) of brosyl chloride, by the method outlined for the preparation of 2-deuterio-5,5-dimethyl-5-sila-2-hexyl brosylate: ^{1}H NMR (CDCl$_3$, 60 MHz) δ −0.01 (s, 9 H), 0.45 (br s, 2 H), 4.60 (br s, 1 H), 7.70 (s, 4 H).

1,1,1-Trideuterio-5,5-dimethyl-5-sila-2-hexyl *p*-Bromobenzenesulfonate (Brosylate). 1,1,1-Trideuterio-5,5-dimethyl-5-sila-2-hexyl brosylate (approximately 0.6 g, 50% yield) was prepared from 0.50 g (0.0033 mol) of 1,1,1-trideuterio-5,5-dimethyl-5-sila-2-hexanol and 0.77 g (0.0030 mol) of brosyl chloride, by the method outlined for the preparation of 2-deuterio-5,5-dimethyl-5-sila-2-hexyl brosylate: ^{1}H NMR (CDCl$_3$, 360 MHz) δ −0.062 (s, 9 H), 0.36 (m, 2 H), 1.52 (m, 2 H), 4.568 (br t, J = 6.1 Hz, 1 H), AA′BB; A = A′ = 7.679, B = B′ = 7.773, (d of d, J_{AB} = $J_{\text{A'B}}$ = 10.0 Hz, 4 H).

(*R*)-(+)-Enriched 5,5-Dimethyl-5-sila-2-hexyl *p*-Bromobenzenesulfonate (Brosylate). (*R*)-(+)-Enriched 5,5-dimethyl-5-sila-2-hexyl brosylate (approximately 1.0 g, 44% yield) was prepared from 1.00 g (0.0068 mol) of (*R*)-(−)-enriched 5,5-dimethyl-5-sila-2-hexanol and 1.57 g (0.0061 mol) of brosyl chloride, by the method outlined for the preparation of 2-deuterio-5,5-dimethyl-5-sila-2-hexyl brosylate: specific rotation, 4.56° (589 nm sodium), 4.74° (578 nm mecury), 5.50° (554 nm mercury), 9.845° (436 nm mercury), 16.589° (365 nm mercury); ^{1}H NMR (CDCl$_3$, 360 MHz) δ −0.059 (s, 9 H), 0.35 (m, 2 H), 1.258 (d, J = 6.12 Hz, 3 H), 1.53 (m, 2 H), 4.582 (q of t, J_1 = J_2 = 6.1 Hz, 1 H), AA′BB′A = A′ = 7.679, B = B′ = 7.773 (d of d, J_{AB} = $J_{\text{A'B'}}$ = 10.0 Hz, 4 H).

Conductivity Water. Deionized water was prepared by the procedure described by Murr.[34]

Ethanol (E) was prepared by the procedure described by Murr,[34] with modifications by Buddenbaum.[35]

2,2,2-Trifluoroethanol (TFE or T) was prepared by the procedure described by Shiner et al.[36]

1,1,1,2,2,2-Hexafluoro-2-propanol (HFIP or H) was prepared by the procedure described by Seib.[37]

Ethanol–Water. These volume percent solutions were prepared by weight using densities and bouyancy corrections as described by Murr.[34]

2,2,2-Trifluoroethanol–Water. These solutions were prepared as weight percent solutions by the method described by Shiner et al.[36]

1,1,1,2,2,2-Hexafluoro-2-propanol–Water. These solutions were prepared as weight percent solutions by the method described by Seib.[37]

Conductance Kinetics Procedure. Conductance measurements were taken by using a bipolar pulsed conductance apparatus built in this laboratory based on the design of Caserta and Enke.[18] This instrument was calibrated by comparing the experimental resistances with known fixed resistors and fitting the curve to a eight-parameter equation using the simplex method.[38] Conductivity cells used were made in this laboratory based on the design of Murr,[34] using modifications by Dowd,[39] Tomasik,[40] and Wilgis.[41] The data were recorded by a TI 980 computer using programs developed by McMullen[42] and Tomasik.[40] The data were analyzed on a IBM PC using a calibration program written by Tomasik[40] and Wilgis[41] and a nonlinear, doubly weighted least-squares program written by Buddenbaum[35] with modifications by Vogel,[43] Pinnick,[44] Bowersox and Tomasik,[45] and Wilgis.[41] The first program converts instrument readings to resistance values by using the eight-parameter calibration equation, while the second (a) converts resistance values to concentrations of ionized *p*-bromobenzenesulfonic acid in solution by using the limiting conductance equation and independently determined values of Λ_0 and $S\alpha$ and (b) fits values of concentrations and clock

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(45) Bowersox, K. D.; Tomasik, M. J., unpublished results.

reading to the first-order rate equation.

Polarimetric Kinetic Procedure. Polarimetric measurements were taken on a Perkin-Elmer Model 241 polarimeter. Kinetic data were collected by a TI 980 computer using programs written by McMullen[42] and Tomasik.[40] The data were analyzed on an IBM PC using the same nonlinear, doubly weighted least-squares program mentioned above but assuming that the observed rotations are directly proportional to concentrations.

The kinetics measurements were taken by using a 10-cm quartz cell fitted with a water circulation jacket and maintained at a temperature of 25 °C with water circulated from a constant-temperature bath.[37]

A typical procedure for doing a kinetic experiment is as follows. The desired amount of compound was weighted into a 1-mL volumetric flask. The flask was filled to the mark with the solvent of choice, and the compound was dissolved by vigorous shaking or by use of a small stirring bar. The reacting solution was placed into a previously cleaned cell (rinsed several times with chloroform and dried with dry argon) and stoppered. The cell was placed in the instrument, and the circulating hoses were attached. Data collection was initiated after waiting approximately 5 min for an equilibrium temperature to be reached.

Product Determination. Product studies by ^{2}H NMR spectroscopy were performed in the following manner. A 1.0-mL sample of the reaction mixture (approximately 0.1 M in deuterium) was prepared in a 1.0-mL volumetric flask with a molar excess of 2,6-lutadine. This was transferred to a NMR tube, sealed, and allowed to react for more than 10 half-lives. The ^{2}H spectra were recorded using a Nicolet 360 MHz spectrometer at 55.4 MHz. The fourier transform NMR spectra were taken using between 500 and 1000 scans. Product ratios were determined by comparison of the weighed cutouts of the peaks.

Chemical shifts for products, which vary slightly with solvent, are as follows in 97T: 4-(trimethylsilyl)-2-butanol-*2-d*, δ 3.84; 4-(trimethylsilyl)-2-butyltrifluoroethyl-2-*d* ether, δ 3.69; methylcyclopropane-*1-d*, δ 0.78.

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A Spectacular Example of the Importance of Rotational Barriers: The Ionization of Meldrum's Acid[1]

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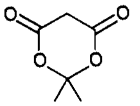
Abstract: The free energy of ionization of Meldrum's acid (I) is 11.68 kcal/mol more spontaneous than that of its acyclic analogue, dimethyl malonate. This energy difference must represent one of the *largest stereoelectronic effects in the literature of organic chemistry* and demands careful elucidation. This paper probes the problem by comparing the effects of various structural contributions to the carbon acidity of Meldrum's acid. The most dramatic effect results from increasing the size of the bislactone ring system. There is a rapid decrease in acidity between the 6-membered and 10-membered ring until the 13-membered ring has the same pK_a as dimethyl malonate. The obvious conclusion from the assembled results is that the difference between the acidities of Meldrum's acid and the larger ring bislactones or diesters lies in the barrier to rotation around the ester bonds. Over half of the 11.68-kcal/mol effect may be explained empirically through the 3–4-kcal/mol stabilization of the *Z* conformation of esters relative to the *E* conformation. Another 3 kcal/mol may be assigned to the cyclization effect seen also in the β-diketone series.

Meldrum[2] produced a product from the condensation of malonic acid and acetone which was so acidic that its structure was wrongly assigned as a carboxylic acid for 40 years until Davidson and Bernhard[3] showed it to be the bislactone I. The pK_a of I in water is 4.83, putting it close to acetic acid and so far above all other α-carbonyl carbon acids that it could not be compared to them quantitatively using the classical aqueous pH scale.



Meldrum's acid (I)

Recently we[4] used Bordwell's DMSO/DMSYL system[5] to relate I to other well-known carbon acids such as the β-diesters represented by dimethyl malonate or the cyclic diketone, dimedone. The salient facts are summarized in Figure 1. Surprisingly, the effect of cyclizing the β-diester system from dimethyl malonate (pK_a = 15.87) to the bislactone I (pK_a = 7.32) reduced the standard free energy of ionization, $\Delta G°_i$, by 11.68 kcal/mol while the corresponding comparison for the acyclic β-diketone, acetylacetone (pK_a = 13.33) with dimedone (pK_a = 11.16) is only 3.07 kcal/mol. Thus, Meldrum's acid has a free energy of ionization that is over 5 kcal/mol more spontaneous than would be expected based on the cyclization of the diketone system. We related this remarkable result[4] empirically to the conformationally dependent dipole moments seen in a series of lactones by Huisgen and Ott[6] and theoretically to Deslongchamps orbital interpretation.[7]

Like other esters and lactones, I does not enolize in solution or in the crystalline state.[8,9] In contrast, its diketone analogue, dimedone, is totally enolized.

The question of the conformation of the ring has long been a matter for speculation and has now been settled, at least for the crystal, as being a boat.[9] Interestingly, a molecular mechanics

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[1] Part 6: Arnett, E. M.; Maroldo, S. G.; Schriver, G. W.; Schilling, S. L.; Troughton, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 2091. The present article may be regarded as part 7 in this series.

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[7] Professor Samuel Danishefsky is presently trying to prepare the seven-membered homologue of I but to date all attempts have failed.

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