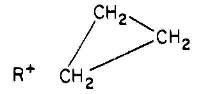
strongly favors the trans-perpendicular structure. Judging from the CC bond lengths, this is not because of improved hyperconjugation. Rather, the C_α–C_γ distance is greatly shortened compared to CH_3, because of an enhanced tendency toward ring closing with SiH_3. Thus, the silyl group causes a new resonance structure to become important. Figure 1 shows the trans-perpendicular silyl structure resulting from the 6-31G* calculation.

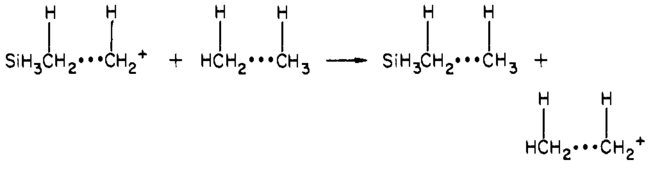
Inspection of the Mulliken charges on the CH_2 groups in Table II clarifies what is happening. The silyl group exerts a large inductive effect on the adjacent CH_2. In the trans-perpendicular conformation this negative CH_2 is able to bond directly to the positive cation carbon to form a closed cyclopropane-like structure. Thus in addition to the usual hyperconjugation resonance structures,

$$R{-}CH_2{-}CH_2{-}CH_2^+ \leftrightarrow R{-}CH_2^+\cdots CH_2{=}CH_2$$

one must also consider the ionic structure



For Li this latter structure completely dominates, and geometry optimization leads to edge-lithiated cyclopropane with a huge, orientation-specific stabilization energy. Because of the electropositive nature of SiH_3, the edge-silylated structure is also considerably stabilized relative to edge-protonated or edge-methylated cyclopropane. This resonance structure will continue to exert a strong effect even for very long intervening chains provided the carbon adjacent to silicon can get close to C_α. Since connection by a long intervening chain is equivalent to no connection at all, a hint of the asymptotic limit can be seen from the fact that $SiH_3CH_3\cdots CH_3^+$ is stabilized relative to H^- exchange with $HCH_3\cdots CH_3^+$



$$SiH_3\overset{H}{\overset{|}{C}}H_2\cdots\overset{H}{\overset{|}{C}}H_2^+ + H\overset{H}{\overset{|}{C}}H_2\cdots\overset{H}{\overset{|}{C}}H_3 \longrightarrow SiH_3\overset{H}{\overset{|}{C}}H_2\cdots\overset{H}{\overset{|}{C}}H_3 + H\overset{H}{\overset{|}{C}}H_2\cdots\overset{H}{\overset{|}{C}}H_2^+$$

by 39.1 kcal/mol while $CH_3CH_3\cdots CH_3^+$ is stabilized by only 1.5 kcal/mol in this comparison.

These model calculations have provided a straightforward theoretical explanation of the otherwise surprising experimental results. They characterize for the first time a general intramolecular mode of electronic interaction whereby electropositive substituents in the γ-position can stabilize carbonium ions.

Acknowledgment. This work was partially supported by NSF Grant CHE-84-13552 and used VAX11-780 and FPS 164 computers whose purchase was partially funded by NSF Grants CHE-83-09446 and CHE-84-05851.

Registry No. $(CH_2)_3{\cdot}H^+$, 17806-70-1; $CH_3CH^+CH_3$, 19252-53-0; $CH_3CH_2CH_2^+$, 19252-52-9; $CH_3CH_2CH_2OH$, 71-23-8; $CH_3CH_2CH_3$, 74-98-6; $(CH_2)_2CH(CH_3){\cdot}H^+$, 27733-92-2; $CH_3CH_2CH_2CH_2^+$, 25453-90-1; $CH_3CH_2CH_2CH_2OH$, 71-36-3; $CH_3CH_2CH_2CH_3$, 106-97-8; $(CH_2)_2CH(SiH_3){\cdot}H^+$, 101932-92-7; $SiH_3CH_2CH_2CH_2^+$, 101932-93-8; $SiH_3CH_2CH_2CH_2OH$, 75967-15-6; $SiH_3CH_2CH_2CH_3$, 13154-66-0; $LiCH_2CH_2CH_2^+$, 101932-94-9; $LiCH_2CH_2CH_2OH$, 101932-95-0.

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(10) The effect of polarization basis functions and electron correlation have been considered for the four critical structures—silyl and methyl, tra-per and tra-pla. For methyl the trans-perpendicular structure is 3.8 kcal/mol below the trans planar at the 6-31G RHF level. This increases to 4.5 kcal/mol at the 6-31G* RHF level and increases further to 8.1 kcal/mol when electron correlation is included (with the 6-31G* basis set). For silyl the perpendicular form is 12.3 kcal/mol more stable with 6-31G RHF, 15.0 kcal/mol more stable with 6-31G* RHF, and 25.1 kcal/mol more stable when electron correlation is included. This larger correlation effect is associated with the increased resonance between the Si^+ and C^+ structures. The electron correlation in these examples was computed by using our standard MRSD-CI method with perturbation extrapolation to the basis set limit.

Liquid-Crystalline Solvents as Mechanistic Probes. 22. The Influence of Smectic Order of *n*-Butyl Stearate and Lyotropic Gels on the Diastereomeric Ratio of Cyclobutanols from the Norrish II Reactions of Aliphatic, Linear Ketones[1]

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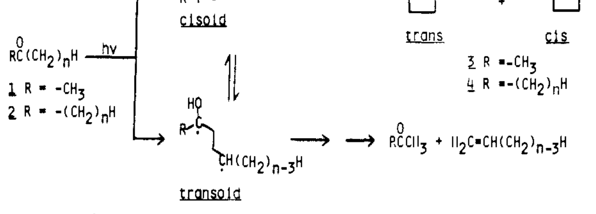
Recently, we demonstrated that liquid-crystalline solvents are capable of mediating the dynamics of 1,4-biradicals generated during the Norrish II reactions of ketones.[1,2] In this work, we examine the Norrish II reaction (eq 1) of a series of 2- and



sym-n-alkanones (**1** and **2**) in the smectic B phase of *n*-butyl stearate (BS) and in the smectic B-like 50% aqueous gel phases of potassium stearate (KS), potassium palmitate (KP), and an equimolar mixture of potassium stearate/1-octadecanol (KSO).[3a,4]

Alkanones with chains longer than 12 carbons exhibit Norrish II quantum efficiencies which are relatively insensitive to temperature and solvent viscosity; their singlet and triplet reaction components maintain a nearly constant ratio.[5] For ketones like **1** and **2**, available evidence indicates that the cyclization products **3** and **4** emanate from cisoid 1,4-biradicals, and elimination products arise primarily from transoid 1,4-biradicals.[2a,6] The ratio of cyclobutanol diastereomers is controlled by a combination of intramolecular steric effects and intermolecular medium influences.

The use of lyotropic gels as a new type of ordered medium for investigating solute reactivity offers a well-characterized bridge between nonaqueous liquid crystals and more disordered lyotropic systems (lipid bilayers, vesicles, and micelles). Even within the gels, gradations of order are apparent from measures of Norrish II reactivity of the solutes. In fact, we find that the trans/cis ratio of diastereomeric cyclization products[7] (**3** or **4**) depends much

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(7) Samples of **1** or **2** in N_2-saturated KS, KP, or KSO (sealed in 1.5–1.8 mm o.d. Kimax capillary tubes) and solutions of **2** in BS (sealed under vacuum in 0.8 mm i.d. Pyrex cells) were irradiated in a thermostated water bath with a quartz-filtered 450-W medium-pressure Hg Hanovia lamp. Conversions of the ketones were approximately 10–15%. The ketones and products were extracted from the gels with ether prior to analyses. Extractions and analyses of gels, doped with known proportions of ketones and products, were conducted to ensure the validity of the procedures. The extracts and the BS samples were analyzed by gas chromatography. The assignments of *trans*- and *cis*-cyclobutanols is based upon both the relative retention times and the relative yields of the two diastereomers (as obtained in isotropic solvents). (a) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506. (b) Casal, H. L.; de Mayo, P.; Miranda, J. F.; Scaiano, J. C. *Ibid.* **1983**, *104*, 6959. (c) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *Ibid.* **1983**, *105*, 6959. (d) Turro, N. J.; Liu, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413.

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Table I. Trans/Cis Ratios for Cyclobutanols from Irradiations of **1** and **2** in Various Media

ketone	hexane (25 °C)	*t*-BuOH (25 °C)	isotropic BS (30 °C)	smectic BS (20 °C)	KP (25 °C)	KS (38 °C)	KSO (38 °C)
1, *n* + 2							
11[a]	1.5 ± 0.1	1.0 ± 0.1	1.2 ± 0.2	1.3 ± 0.2			
13		1.5 ± 0.1			0.43 ± 0.01	0.37 ± 0.03	0.91 ± 0.2
15	2.8 ± 0.1	1.2 ± 0.1			0.42 ± 0.04	0.40 ± 0.03	1.1 ± 0.2
17	3.1 ± 0.2	1.3 ± 0.1			0.48 ± 0.05	0.56 ± 0.05	1.1 ± 0.2
19		1.3 ± 0.1			0.59 ± 0.03	0.71 ± 0.04	
2 (2*n* + 1)							
11		2.0 ± 0.2	1.8 ± 0.5	1.5 ± 0.5			
13	2.9 ± 0.1	2.2 ± 0.1			2.2 ± 0.1	2.1 ± 0.2	4.6 ± 0.6
15		1.5 ± 0.2	2.4 ± 0.6	2.8 ± 0.5	3.0 ± 0.2	2.9 ± 0.4	8.5 ± 0.5
17	2.7 ± 0.2	1.3 ± 0.1	2.2 ± 0.6	10.8 ± 1.6	1.7 ± 0.1	5.6 ± 0.8	12.7 ± 1.5
19		1.3 ± 0.2	1.8 ± 0.2	13.3 ± 0.3	2.1 ± 0.1	2.0 ± 0.4	3.5 ± 0.5
21	3.2 ± 0.2	1.2 ± 0.2	2.5 ± 0.6	14.1 ± 1.0		2.2 ± 0.3	
23		1.3 ± 0.1				2.0 ± 0.4	
25	3.2 ± 0.2	2.0 ± 0.1				0.22 ± 0.04	3.2 ± 0.1

[a] Reference 2.

more critically upon the location of the carbonyl group in the solute molecules and the relationship between the total lengths of the solvent and solute chains than had been appreciated previously.

The smectic B phase of BS has been characterized by X-ray, infrared, and NMR techniques.[3] The thickness of each layer is the length of an extended BS molecule. Lyotropic gels (β phases) are much more ordered and much less fluid than typical lyotropic liquid crystals (α phases).[8a] Skoulios and co-workers have measured the thickness of the water-separated amphiphilic layers of KS, KP, and KSO.[4] They find that the head groups in KS and KP alternate head to tail and the chains are nearly completely interdigitated: the thickness of a layer is slightly longer than an extended acid molecule. KSO consists of bilayers in which stearate and 1-octadecanol molecules alternate within a layer. The average distance between mono- or bilayers of organic material in the gels is controlled by the weight fraction of water present. The arrangements are depicted in Figure 1.

Both thermochemical and spectroscopic studies in other mesophases indicate that the closer the size and shape of a solute to the solvent, the more completely will the average residence of the solute resemble that of a constituent solvent molecule.[9] On this basis, and given their low concentration (1% by weight of BS or amphiphile), solutes **1** and **2** are expected to be well dispersed within the smectic B layers, such that their long axes are parallel to those of the solvent. Furthermore, the reactive chromophores of **1** will experience an environment near the more polar and disordered parts of a phase layer while the carbonyls of **2** will reside closer to the more lipophilic and ordered middle of a phase layer.[3]

The degree to which this difference in local polarity and order affects solute reactivity is evident upon comparison of the trans/cis ratios of cyclobutanols from **1** and **2** (Table I). The expected ratios of **3** and **4** in completely disordered solvents are taken in the isotropic phase of BS, in hexane, or in *tert*-butyl alcohol. The lack of appreciable influence of the three gels on the ratios of **3** is apparent: increased polarity and/or disorder near the solvent chain ends where the chromophores reside is sufficient to allow the motions of the intermediate 1,4-biradicals leading to *trans*- or *cis*-**3** to be invariant to the chain length of **1**.

By contrast, the ratios of **4** experience changes which maximize when the number of methylenes in the gel molecules and the number of carbons in **2** are equal. However, the order of the gels exerts no detectable influence on the dynamics of cisoid 1,4-biradicals from **2** which are slightly shorter or slightly longer than the hydrophobic portion of the amphiphiles! The magnitudes of the maximal increases in the ratios of **4** parallel what is known to be the sequence of order among the gel phases. For instance, KSO is a more demanding matrix than KS: addition of 1-alkanols to lamellar phases is known to "stiffen" them.[8b,c] In smectic BS, an abrupt increase in the trans/cis ratio of **4** occurs when the number of solute carbons and the number of stearoyl methylenes (17) are equal; thereafter, the ratios increase slowly and approach (what appears to be) a plateau value.

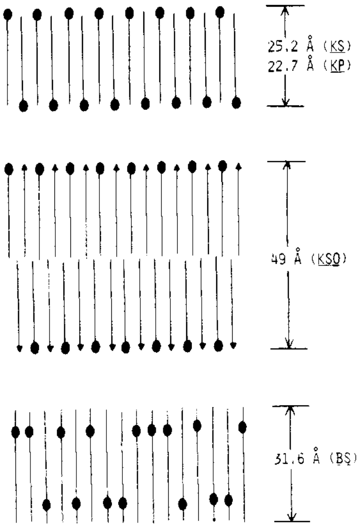

Figure 1. Side-on view of gel and BS smectic layers. The carboxy (●), hydroxy (▲), and chains (—) are shown in a stylized representation.

The sensitivity of the changes in the trans/cis ratios of **4** in these smectic phases are unparalleled in our experience. We believe that they demonstrate the necessity of a solute to be very near in both shape and size to the constituent molecules if localized fine solute motions like those which control formation of *cis*- or *trans*-**4** from the cisoid 1,4-biradicals of **2** are to be influenced by ordered intermolecular interactions. Solutes of **2** which are shorter than the hydrocarbon portions of the solvent cause disorder in nearby molecules which appears to be transmitted along their chains to the cybotactic region.

Interestingly, preliminary experiments with **2** (2*n* + 1 = 25) yield a trans/cis ratio for **4** in KS of 0.2. This value is reminiscent of ratios obtained for **3** (i.e., from carbonyls reacting near the head groups of the amphiphiles). The ratios of **4** (2*n* + 1 = 25) in *tert*-butyl alcohol (2.0) and KSO (3.2) are "normal" and lead us to believe the solute chain has doubled over in KS, leaving the carbonyl more exposed to a layer interface. Anomalous ratios of elimination/cyclization products from this ketone in KS support our contention.

We are presently pursuing a clearer understanding of these solute length-dependent effects on *trans*-/*cis*-cyclobutanol ratios as well as on other reaction parameters (e.g., elimination/cyclization product ratios, Norrish I vs. Norrish II selectivity, and relative quantum efficiencies). Our studies to date demonstrate the utility of smectic BS and gel phases to detect minor mechanistic

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changes of ketone solutes. It is obvious that many other reactions and processes are amenable to study in these media.

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Hypervalent Silicon Hydrides: SiH_5^-

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The rich diversity and practical utility of organosilicon chemistry continues to engender widespread research interests.[1] A key issue in the field involves the role of the low-lying vacant Si d-orbitals in the properties and reactivity of silicon-containing compounds. A familiar manifestation of d-orbital participation is the aptitude of silicon for hypervalency in the form of (10-Si-5) pentavalent anions.[2] Examples of pentavalent silicon anions have been isolated and structurally characterized,[3] and they are frequently invoked as intermediates in nucleophilic addition reactions of organosilanes in solution.[4-7] Moreover, several 10-Si-5 negative ions bearing alkyl, alkoxyl, and halogen ligands have been identified as products of gas-phase ion-molecule reactions.[8-10] We now wish to report the synthesis and characterization of the archetype pentavalent silicon anion, SiH_5^- (**1**), along with several of its simple alkyl derivatives in a flowing afterglow apparatus at 298 K.[11]

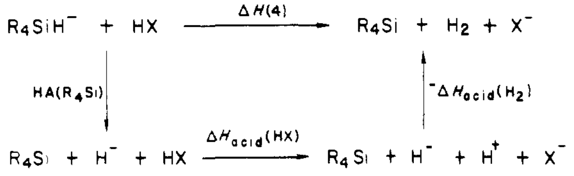
Hydride ion is a potent gas-phase base (PA = 400.4 kcal/mol)[12] which can be generated by electron impact on either NH_3 or CH_4. Its direct reaction with SiH_4 in a flow reactor at 0.4 torr has been previously reported by Bohme and co-workers to yield exclusively SiH_3^- by proton transfer.[13] Interestingly, when D^- is the reactant ion, H^- and SiH_2D^- also appear as products, implying that reversible addition of the nucleophilic ion to silicon occurs during the course of reactive collisions. We have now found that H^- reacts with *alkyl*silanes in a flowing afterglow at 0.4 torr total pressure by exclusive addition (eq 1). These reactions are most likely

$$H^- + R_4Si \xrightarrow[He]{} R_4SiH^- \qquad (1)$$

$$R_4Si = Me_4Si,\ Et_3SiH,\ Et_2SiH_2,\ n\text{-}C_5H_{11}SiH_3$$

saturated termolecular processes as shown by their large bimolecular rate coefficients at 0.4 torr (e.g., 4.5×10^{-9} cm^3 s^{-1} for Et_3SiH) and their pressure-independent product distributions from 0.3 to 0.9 torr. Relative to SiH_4, termolecular addition is facilitated in the larger alkylsilanes by the greater complexity and, thus, longer lifetimes of the intermediate collision complexes.[14] Adduct formation appears to be unique to hydride ion since other strongly basic anions such as NH_2^- (PA = 403.6 kcal/mol)[12] and OH^- (PA = 390.7 kcal/mol)[12] react only by proton abstraction and condensation reactions.[10]

Scheme I



The alkylsilyl hydride anions formed by reaction 1 behave as potent hydride donors, reducing a wide variety of substrates in bimolecular hydride transfer reactions such as CO_2, Et_3B, and $Fe(CO)_5$.[15] Of special significance is the observation of facile hydride transfer among the silanes themselves. In particular, both $n\text{-}C_5H_{11}SiH_4^-$ (**2**) and $Et_3SiH_2^-$ (**3**) transfer hydride to SiH_4 to produce the parent ion of the series, SiH_5^- (eq 2). The major

$$\underset{\mathbf{3}}{Et_3SiH_2^-} + SiH_4 \xrightarrow{68\%} \underset{m/z\ 31}{SiH_3^-} + Et_3SiH + H_2$$
$$\xrightarrow{32\%} \underset{\substack{m/z\ 33\\ \mathbf{1}}}{SiH_5^-} + Et_3SiH \qquad (2)$$

primary product with $Et_3SiH_2^-$ is SiH_3^- (68%), which is also observed to build up as a secondary product at the expense of SiH_5^- at higher SiH_4 flow rates. This latter observation indicates that an 'autocatalyzed' decomposition reaction is occurring (eq 3). The

$$SiH_5^- + SiH_4 \rightarrow SiH_4 + H_2 + SiH_3^- \qquad (3)$$

occurrence of such a reaction in the gas phase requires that SiH_5^- be thermodynamically unstable with respect to H_2 dissociation but may survive intact under the present conditions by virtue of a kinetic barrier preventing prompt fragmentation. Computational studies of SiH_5^- support this conclusion since it has been determined at quite high levels of theory that although H_2 dissociation is ca. 6 kcal/mol exothermic, a D_{3h} trigonal-bipyramidal SiH_5^- structure represents a local minimum on the potential energy surface.[16-19]

Reaction 3 is but one example of a more general protolytic reaction which may occur between silyl hydride anions and Brønsted acids (HX) (eq 4). We have exploited this reaction

$$R_4SiH^- + HX \rightarrow [R_4\overset{\delta^-}{Si}\cdots H\cdots H\cdots \overset{\delta^-}{X}] \rightarrow R_4Si + H_2 + X^- \qquad (4)$$

in the determination of thermochemical data for SiH_5^- and two of its alkyl derivatives. Equation 4 may be formulated in terms

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