of Chiang and Chang.[19] During the preparation of this paper, X-ray crystallographic and chemical studies revised the structures of soyasapogenols B and E to **1** and **3**, respectively.[20] This paper demonstrates that delayed correlation spectroscopy permits this assignment in a few simple experiments. Variation in the delay time, coupled with a relatively short acquisition time (100-200 ms), simplifies the 2-D maps by enhancing cross peaks of desired *J* magnitude and allows proton assignments in highly congested regions of the spectrum.

The oleanene triterpene **1** is structurally very different from the previously isolated xenognostic flavonoids active in the *Agalinis* system.[8] It is perhaps relevant to the broad host range of this parasite that both **1** (soyasapogenol B) and **3** (soyaspogenol E) appear to be widely distributed in the Leguminosae. Interestingly, although both molecules are present in *Lespedeza sericea* root exudate, **3** does not appear to induce haustorial differentiation in *Agalinis.*

Acknowledgment. We thank W. C. Hutton and Jeffrey Shabanowitz for valuable suggestions during the course of the work and Dr. Mike Thompson for much of the initial biological study. Support from USDA Competitive Research Grant 5901-0410-9-0257, USDA Cooperative Research Agreement 58-7B30-0-196, Research Corp., and Frausch Foundation as well as partial support for the NTC 360 from NSF is gratefully acknowledged.

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Evidence for a Silylenium Ion in Solution

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One of the key organic intermediates that heretofore has not been observed in solution is trivalent, positively charged silicon, the silylenium ion (R_3Si^+, the silicon analogue of the carbenium ion).[2,3] Evidence has been presented for such species in the gas phase,[4,5] but numerous efforts in solution have met with failure.[6,7] Undoubtedly a major contributor to these negative results is the poor ability of silicon to undergo p_π-p_π bonding. Whereas carbenium ions are readily stabilized by 2p-2p resonance, the silylenium ion is more weakly stabilized through 2p-3p overlap over longer bonds with lone pairs or π electrons on carbon, nitrogen, or oxygen.[5] Furthermore, the very large single-bond energies of silicon with oxygen, nitrogen, and most halogens render unavailable many common leaving groups.

Our current strategy is to provide stabilization to the silylenium ion through the use of highly polarizable substituents. Our choice of sulfur (alkylthio) as the substituent on silicon was guided not only by its high polarizability but also by the low electronegativity of sulfur and by the possibility that 3p-3p overlap would be more effective than 2p-3p overlap. After these experiments were well underway, Apeloig[8] and Godleski[8,9] showed by ab initio calculations that HS provides net stabilization to the $XSiH_2^+$ ion (X = HS). The leaving group problem had already been solved by J. Y. Corey, who suggested that silylenium ions could be generated by abstraction of hydride by trityl salts.[10] Maximization of stabilization through polarization and 3p-3p overlap thus suggested that $(RS)_3SiX$ would be an ideal precursor for a silylenium ion, and the Corey procedure required that X must be H. Further polarization could be obtained from the use of a reasonably large alkyl group for R such as isopropyl. Fortunately, tris(alkylthio)silicon hydrides are readily available from the reaction of trichlorosilane with alkanethiols.[11] Consequently, we prepared tris(2-propylthio)silane in this fashion and subjected it to the Corey conditions (eq 1).

$$(i\text{-PrS})_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + (i\text{-PrS})_3Si^+ClO_4^- \qquad (1)$$

Our previous results showed that a wide variety of silanes undergo the Corey reaction to give nonconducting, presumably covalent perchlorates, e.g., Ph_3SiH gives $Ph_3SiOClO_3$.[6] In contrast, a 1/1 mixture of tris(2-propylthio)silane (4.61×10^{-4} mol) and trityl perchlorate, prepared in dilute methylene chloride solution at room temperature, gave a solution with a specific conductance of 110.8 μmho cm^{-1}. This value is comparable to that of a fully ionic species such as trityl perchlorate (5.03×10^{-4} mol), which was 102.0 μmho cm^{-1}. An analogous solution of triphenylsilane (6.86×10^{-4} mol) and trityl perchlorate had a specific conductance of only 2.2 μmho cm^{-1}.

Nuclear magnetic resonance spectra of the ionic species in CD_2Cl_2 (about 0.8 M) were extremely clean. The ^{13}C spectrum showed only a single pair of isopropyl resonances (δ 27.1 and 37.5) in addition to those of triphenylmethane. The ^1H spectrum showed one isopropyl doublet (δ 1.35), one isopropyl septet (δ 3.37), the triphenylmethane methinyl singlet (δ 5.38), and the aromatic resonances. When less than 1 equiv of trityl perchlorate was added, only resonances from the starting material and the single product were observed. Thus, in a titration-type experiment, the loss of the SiH resonance (δ 5.70) and the simultaneous gain of the triphenylmethane methinyl resonance could be followed, as could the loss (δ 1.28, 3.17) and gain (δ 1.35, 3.37) of the appropriate isopropyl methyl resonances. The magnetic resonance experiments showed that (1) only one species is formed, (2) the species has only one type of isopropyl group (or is exchanging rapidly) and no other alkyl group, and (3) the species is formed by removal of the hydride on silicon, because of loss of SiH and gain of triphenylmethane CH.

The ionic species could be further characterized spectroscopically. The electronic spectrum had a single, intense λ_{max} at 352 nm, quite distinct from the values for trityl perchlorate at 410 and 435 nm. The infrared spectrum contained bands characteristic of ionic perchlorates, at 1100 (s) and 620 (m) cm^{-1}, although these are mixed with various other bands. Trityl perchlorate itself has bands at 1095 (vs) and 625 (m) cm^{-1}. The extremely weak ^{29}Si resonance was at 18 ppm to high frequency (low field) of Me_4Si, compared with 1 ppm for the starting material, $(i\text{-PrS})_3SiH$. The lack of nearby protons makes for very slow ^{29}Si relaxation, and the silylenium peak may be unobservable. The observed peak may be from polymer that develops during the 16 h utilized for spectral acquisition. An EPR spectrum (3×10^{-2} M sample) showed no signal. A lower limit to the concentration of radical cations was set at 10^{-9} M. The molecular weight was measured to be 376 ± 22 (theory 353) for two particles in sulfolane.[12]

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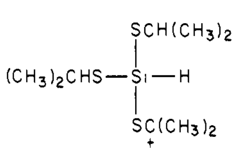
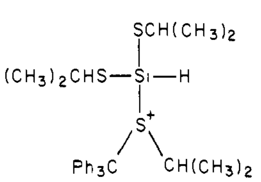
The ionic species does not appear to exhibit appreciable delocalization of positive charge from silicon to sulfur, i.e., the ion is best termed silylenium rather than sulfonium (RS—$^+$Si< ↔ RS$^+$=Si<). This conclusion is reached from the resonance position of the methinyl carbon in the isopropyl group, which shifts only from 36.52 to 37.46 ppm on conversion of the silyl hydride to the ionic species. Development of a full positive charge on sulfur is exemplified by the shift of the methinyl resonance from 33.70 to 44.91 ppm on conversion of diisopropyl sulfide to its methylsulfonium salt. If the shift in the silyl ion (0.94 ppm) is multiplied by 3 because the charge is spread over three sulfurs, the value is still only 25% of that for the full sulfonium ion (11.21 ppm). Since the methyl group in the methylsulfonium salt introduces a β effect of unknown size, we also measured the charge on simple protonation of diisopropyl sulfide (CH at δ 33.37 for neat, neutral sulfide, δ 42.43 for protonated sulfide). The 0.94 ppm shift in the silylenium ion, multiplied by 3, is still only 30% of this value.

Finally, tris(2-propylthio)silane could be recovered upon reaction of the ionic solution at −78 °C with diisobutylaluminum hydride. The silane was distilled from the reaction mixture (**Caution**: overheating can cause an explosion) and found to have ^{1}H NMR and IR spectra identical with those of the starting silane.

The most likely alternative ionic species would involve abstraction of a different hydride (**1**), complexation without abstraction (**2**), or oligomerization (e.g., **3**). The species **1** is eliminated by the ^{1}H and ^{13}C spectra, which contained only one isopropyl resonance; in addition, **1** retains the SiH, which is clearly lost on formation of the ionic species. The sulfonium ion **2** also has multiple isopropyl groups and would have been formed without loss of the SiH, in contradiction to observation. The dimer **3** has two distinct types of isopropyl groups and deviates significantly from the observed molecular weight. Complexation by the solvent CH_2Cl_2 also is unlikely, because it would add appreciably to the molecular weight.



1



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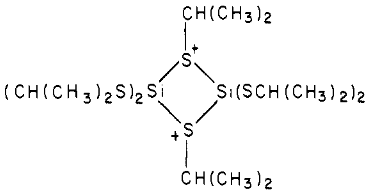

3

In summary, tris(2-propylthio)silane forms a highly conducting solution on reaction with trityl perchlorate. The ^{1}H spectrum shows complete loss of the SiH resonance, concomitant with gain of the triphenylmethane CH resonance. The ^{13}C spectrum shows resonances of only one isopropyl-containing product with chemical shifts appropriate for silylenium rather than sulfonium character. The molecular weight in sulfolane corresponds to a two-particle monomer. Reaction of the ionic solution with diisobutylaluminum hydride yields only recovered tris(2-propylthio)silane. These observations seem most in accord with a silylenium ion structure. The charge on silicon is sustained by the high polarizability, low electronegativity, and 3p lone-pair donating ability of sulfur.

Acknowledgment. We are grateful to Professors R. L. Burwell, Jr. (Northwestern University), and J. Y. Corey (University of Missouri—St. Louis) for useful suggestions.

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Crystal Structure and Solid-State Reactivity of 4,4'-Methylenebis(phenyl isocyanate) (MDI)

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4,4'-Methylenebis(phenyl isocyanate) ($O{=}C{=}N{-}C_6H_4{-}CH_2{-}C_6H_4{-}N{=}C{=}O$, I), a common industrial chemical generally referred to as MDI, has long been known to undergo a reaction in the solid state to give higher molecular weight products formed by intermolecular reaction of the isocyanate groups. The reactivity of MDI has been of particular interest both because it provides a rare example of a reaction that is more rapid in the ordered solid state than in the melt[1] and because little is known about the solid-state chemistry of organic isocyanates. The decreased reactivity of MDI in the melt has been of some industrial importance; Prosser and Seibert have obtained a patent[2] based on the observation that storage of MDI could be improved by keeping it just above its melting point of 42 °C. to minimize the unwanted solid-state reaction. The crystal structure of MDI had not been investigated, and in fact, little is known about the crystal structures of simple isocyanates,[3,4] in part at least because the common members of the family tend to have low melting points and hence do not exist as crystalline solids at room temperature. This communication reports the crystal structure of MDI (I) and examines the relationship of the structure to observed solid-state reactivity.

A crystal suitable for X-ray diffraction was obtained by slow evaporation of a hexane solution, and the structure, determined from data collected at room temperature, is shown in Figure 1.[5] The molecule lies on a crystallographic 2-fold rotation axis; a most significant feature is that adjacent molecules have isocyanate groups related by an inversion center with intermolecular N--C contacts of only 3.146 (2) Å and with adjacent antiparallel N=C atom pairs forming an approximate square. The phenyl rings attached to the nitrogen atoms of the incipient azetidione ring are nearly in the plane of the four atoms forming that ring.

To investigate the nature of the reaction product from MDI in the solid state, we examined the infrared spectrum of the solid formed after a sample of MDI had stood for 2 years at ambient temperature in the dark.[6,7] In addition to strong absorption at

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(5) A colorless monoclinic 12-sided irregular prism approximately 0.52 × 0.40 × 0.28 mm, space group *C*2/*c*, $a = 9.974$ (2) Å, $b = 8.331$ (2) Å, $c = 15.199$ (3) Å, $\beta = 92.25$ (2)°, $V = 1262.0$ (5) Å^3, $Z = 4$, mol wt 250.26, ρ(calcd) = 1.318 g cm^{-3}, λ(Mo Kα) 0.71069 Å, was employed. The space group *C*2/*c* was chosen over *Cc* by a comparison of refinements in the two possibilities. The structure was solved by using 1109 independent reflections (785 observed) [$I > 3\sigma(I)$] measured on a Syntex P2$_1$ automated diffractometer in the range 2θ 2–50°. Data were scaled according to behavior of standard intensities and corrected for Lorentz and polarization effects, but corrections for absorption and/or extinction were not warranted. The structure was solved by direct phasing methods using the MULTAN 80 program (P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M. M. Woolfson) and refined by using SHELX 76 (G. M. Sheldrick). Scattering curves, including anomalous dispersion corrections, were taken from the analytical expressions in "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, AL; Vol IV. Refinement converged at $R = 0.036$ and $R_w = 0.046$. The atomic coordinates appear in the supplementary material.

(6) Spectra were measured on Nujol mulls by using a Perkin-Elmer Model 137B Infracord or a Nicolet Model 7000 FT IR instrument.

(7) An estimate of the rate of self-reaction of solid MDI had been made in the patent previously cited.[2] The fraction of reaction calculated from the fraction of toluene-insoluble material was somewhat erratic but was about 1.05%/month at 35 °C and 0.01%/month at 45 °C (mp 42 °C).