Table I. Correlation Coefficients for Linear Relations between Measures of Electronegativity for 21 Main-Group Elements[a]

	ground state in atoms		valence state in molecules	
	μ	V_Q	V_x	X_M
ground state				
μ	1	0.985	0.964	0.951
V_Q		1	0.967	0.945
valence state				
V_x			1	0.989
X_M				1

[a] μ and V_Q are from ref 12; V_x is from ref 3; X_M is from ref 15.

Thirdly, the value of n_x/r_x is dependent on the valence state, charge, and ligand number of the central atom. This means it is general, as in Parr and Pearson's theory. Fourthly and most importantly, there are good linear correlations between V_x and the electronic chemical potential, μ, and the central electrostatic potential, V_Q, at r_μ, for the 21 main-group elements of ref 12. There μ was calculated as the Mulliken electronegativity of a ground-state atom,

$$\mu = (IP + EA)/2 \qquad (2)$$

where IP and EA are the ionization potential and the electron affinity, respectively; r_μ is the radial distance at which the total electrostatic potential, $V(r_\mu)$, of a ground-state atom exactly equals its chemical potential, μ. V_Q is defined as Q/r_μ, where Q is the total electronic and nuclear charge inside a sphere of radius r_μ. The correlation coefficients have been determined, as shown in the second-last column of Table I.

A close linear relation between r_μ and the covalent radius has been noted previously.[12-14] Mulliken's scale of electronegativity, μ, for free atoms in the ground state was found to be strongly correlated with V_Q.[12]

Any atom in a molecule is in its energetically optimum valence state, not in the free ground state. The covalent radius is a particular measure of the size of an atom in a molecule[13] and is thus a valence-state property.

The parameters μ, $V(r_\mu)$, r_μ, and V_Q of atoms in valence states have been too difficult to calculate so far by absolute electronegativity theory. But valence-state ionization potentials, electron affinities, and Mulliken electronegativities have been calculated[15] by the semiempirical method of Hinze and Jaffe.[16] According to absolute electronegativity theory, the inherent Mulliken electronegativity scale, X_M, from the valence-state analogue of eq 2, the electronic chemical potential, μ, and Huheey's[17] parameter, a, are all approximately the same.

We have calculated the correlation coefficients for linear relations between four measures, μ, V_Q, V_x, and X_M, of electronegativity for the 21 main-group elements considered in ref 12. They are listed in Table I.

It is interesting to note in Table I that the two ground-state measures, μ and V_Q, correlate well with each other, but less well with the valence-state measures, V_x and X_M.

The simple V_x is strongly linked with X_M, as shown in Figure 1; the correlation coefficient is 0.989. This comparison means that the new scale, V_x, is theoretically reasonable and a good measure of the valence-state electronegativity. This explains the good correlations between V_x and bonding properties. V_x should be a basic parameter for diatomic and polyatomic properties.[5]

Parr and Pearson's absolute electronegativity theory is sophisticated, and Hinze and Jaffe's method is advanced. The new scale is not only theoretically reasonable and scientifically useful but also so simple that beginning chemistry students know the
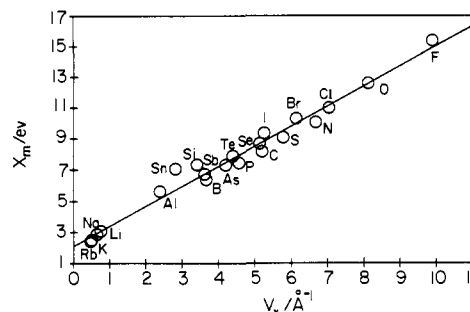
Figure 1. Relation between V_x and the chemical potentials of the valence states, X_M, for 21 main-group elements.

two parameters, n_x and r_x. On the basis of previous work[1-10] and this work, we predict that there is a good possibility (a) of using the new scale to simply correlate energies of polyatomic systems and (b) of introducing and teaching the new scale in introductory classes.

Preparation and Photochemistry of Disilanyl Quinones: Formation of Novel Sila-m-quinomethane Intermediates[1]

Kenkichi Sakamoto and Hideki Sakurai*

Department of Chemistry, Faculty of Science Tohoku University, Aoba-ku, Sendai 980, Japan

Recently, photochemical reactions of organosilicon compounds involving intermolecular charge transfer processes have received considerable attention from both synthetic and mechanistic viewpoints.[2] However, relatively few photoinduced intramolecular charge transfer reactions of organosilicon compounds have been reported.[3] We report herein the preparation and photoreactions of hitherto unknown disilanylbenzoquinones (**1**), an interesting class of organosilicon compounds containing both electron-withdrawing (benzoquinone) and electron-releasing (dislane) groups connected directly to each other.[4] Photochemical reactions of **1** resulted in the formation of novel sila-m-quinomethane intermediates.

2-(Pentamethyldisilanyl)-5-*tert*-butyl-1,4-benzoquinone (**1a**, R = *t*-Bu) was prepared by a series of reactions as indicated in Scheme I. 2-Bromo-5-*tert*-butyl-1,4-bis[(pentamethyldisilanyl)oxy]benzene (**2a**) was treated with 1.1 equiv of *t*-BuLi at −78 °C, and the resulting anion **3a** was warmed slowly to −20 °C. During the course of warming, spontaneous rearrangement occurred to give **4a**, which was oxidized with dichlorodicyanobenzoquinone (DDQ), without isolation, to **1a** in 43% overall

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(3) [(Trimethylsilyl)methyl]-1,4-benzoquinone may be structurally related to **1** in view of the possible $\sigma(Si-C)-\pi$ conjugation. However, no photochemical reaction has been described. Karabelas, K.; Moore, H. W. *J. Am. Chem. Soc.* **1990**, *112*, 5372.
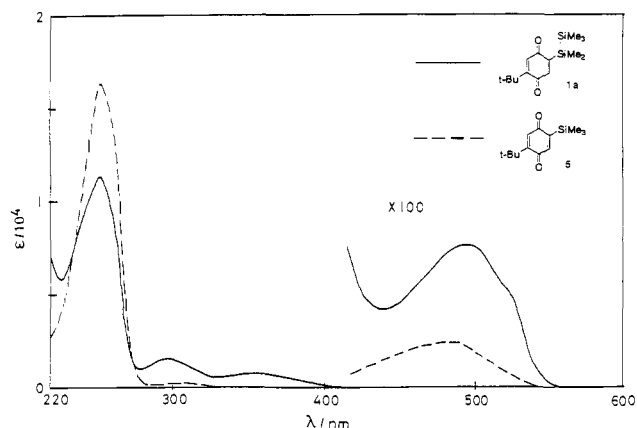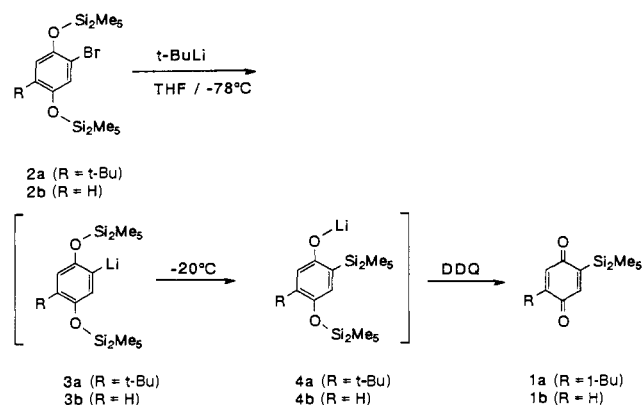(4) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837.

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Figure 1. Electronic absorption spectra of **1a** and **5**.

Scheme I

yield.[5,6]   The unsubstituted derivative **1b** (R = H) was also obtained in 12% yield by a similar method.

2,5-Bis(pentamethyldisilanyl)-1,4-benzoquinone (**1c**) was derived similarly from 2,5-dibromo-1,4-bis[(pentamethyldisilanyl)oxy]benzene in 21% yield. All these compounds, obtained as orange red crystals, were sensitive to diffused light. Unsubstituted compound **1b** was especially unstable and decomposed within a few days at room temperature even in the dark. However, **1a** and **1c** are relatively stable and can be stored in the dark over several months without appreciable decomposition.

The electronic absorption spectra of **1a** and a reference compound, 2-*tert*-butyl-5-(trimethylsilyl)-1,4-benzoquinone (**5**) are shown in Figure 1. Both compounds have two p → π* absorption bands at about 250 and 300 nm and n → π* absorption bands at about 500 nm.[7] However, **1a** has another broad absorption band centered at 350 nm, which can be assigned to a σ(SiSi) → π* charge transfer (CT) transition.

Because of the existence of such an intramolecular CT interaction, disilanylbenzoquione was expected to react photochemically. Indeed, interesting novel photochemical reactions were observed as follows. Irradiation (λ > 520 nm) of a hexane solution of **1** in the presence of a variety of ketones (acetone, benzophenone, and fluorenone) under argon gave a yellow solution. The color of the solution faded completely within 10 min at room temperature. Evaporation of the mixture followed by silica gel chromatography afforded colorless adducts **6** in almost quantitative yields. In the presence of alcohols (methanol and *tert*-butyl alcohol), however, no such colored species was formed and instead adducts **7** were obtained quantitatively.[8]
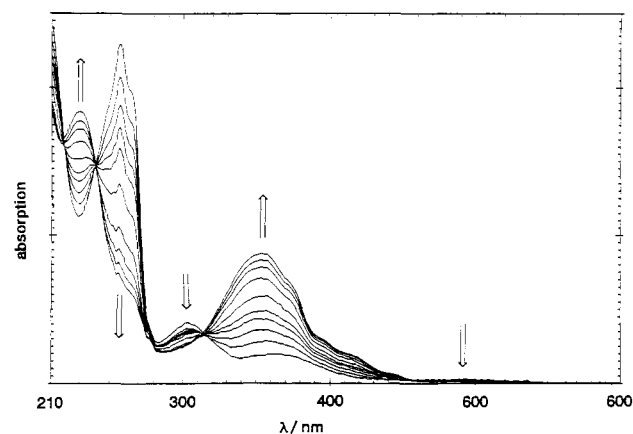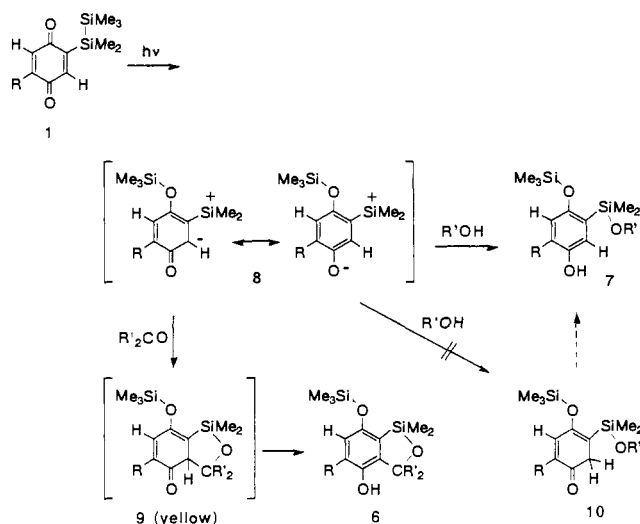
Figure 2. Absorption spectral changes during photolysis of **1c** in a 3-MP matrix at 77 K.

Scheme II

The reaction can be interpreted most satisfactorily in terms of the intermediacy of sila-*m*-quinomethane **8**, which gives a 1,3-adduct **9** by the reaction with ketones. The intermediate **9**, which should be responsible for the yellow color of the solution, was a keto form of the phenol and isomerized to **6** easily. For the reaction with alcohols, **7** was obtained by 1,5-addition directly. The possibility of the 1,3-addition to form **10**, followed by proton transfer to give **7**, was excluded by an experiment with CH₃OD; i.e., photolysis of **1** in the presence of CH₃OD gave the adduct **7** in which no deuterium was incorporated in the aromatic ring (Scheme II).

The key intermediate **8** was isolated in a matrix at 77 K. A 3-methylpentane (2-MP) solution of **1a** was irradiated at 77 K to give a yellow species. The change of the absorption spectra was monitored as shown in Figure 2. New strong peaks centered at 230 and 340 nm appeared according to the progress of irradiation. These peaks disappeared when the matrix was annealed. Photolysis of **1a** in a 3-MP matrix containing a small amount of methanol at 77 K gave the same yellow species, which gave **7a** (R' = CH₃) after the matrix was annealed. Therefore the yellow species was identified as the intermediate **8a**. The matrix containing **8** shows no triplet ESR signal, indicating that **8** is a singlet at the ground state, in contrast with *m*-quinomethane, which has a triplet ground state.[9] The observation that **8** was not a triplet

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biradical but a single zwitterion was in good accord with the chemical reactivities described above. Further investigations of the new intermediate sila-*m*-quinomethane are in progress.

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Configuration, Conformation, and Colligative Properties of a Phosphorus-Stabilized Anion

Scott E. Denmark,* Paula C. Miller, and Scott R. Wilson[†]

Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801

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As part of a general program to develop chiral, phosphorus-based anionic reagents,[1] we required an accurate model of the structure and bonding in these species to guide the design of auxiliaries.[2] Apart from the pioneering spectroscopic studies on Horner–Wittig reagents by Kirilov[3] and Seyden-Penne,[4a-c] the structure of phosphorus-stabilized anions (excluding ylides) has been little investigated.[4d-h,5]
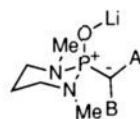
Li⁺**1a⁻**: A = H; B = Ph
Li⁺**1b⁻**: A = B = CH₃

We have recently reported the first X-ray crystal structure determination[6-8] of a phosphoryl-stabilized anion, Li⁺**1a⁻**, which

[†] Correspondence author for inquiries concerning the X-ray structure determination.

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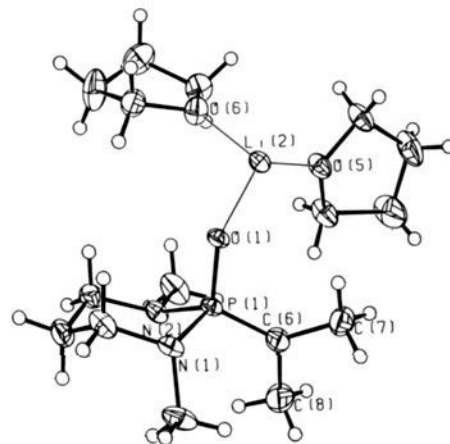(6) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864.

Figure 1. Crystal structure of [Li⁺**1b⁻**]₂·4THF at –75 °C; monomer unit shown for clarity (35% thermal ellipsoids).
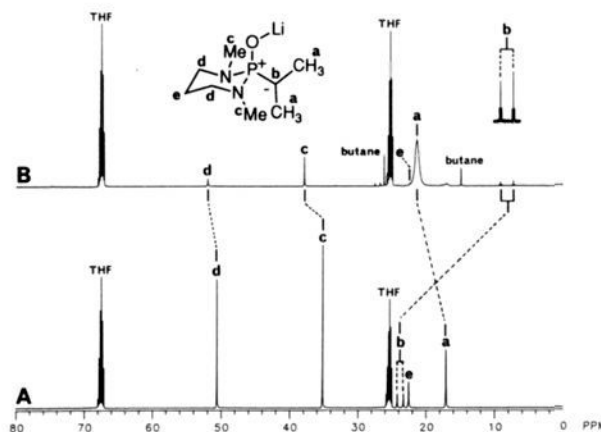

Figure 2. ¹³C NMR spectra (125.8 MHz) at –100 °C. Spectrum A: **1b** (neutral, natural abundance). Spectrum B: Li⁺**1b⁻** (anion, 50% ¹³C-enriched in one *C*-methyl group).

Table I. Planarity Criteria for C(6) (Mean Values)[a]

anion	A	B	|α| + |β|, deg	Σ, deg	γ, deg	d, Å
Li⁺**1a⁻**	H	Ph	171.1 (35)	359.4 (60)	7.3	0.06
Li⁺**1b⁻**	CH₃	CH₃	165.4 (9)	358.5 (7)	11.6	0.11

[a] The sum of the torsion angles (|α| + |β|); the sum of all angles about C(6) (Σ); the angle of the C(6)–P(1) vector to the C(6)–A–B plane (γ); the distance of C(6) to the A–P(1)–B plane (d).

established, inter alia, the planarity and preferred conformation of the carbanionic carbon. In this report we disclose crystallographic and NMR analyses of the related *P*-isopropyl anion Li⁺**1b⁻**

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