Ab Initio Study on the Effects of the Substituent and the Functional Group on the Isomerization of $H_3CC(X){=}Y$ and $H_2C(X)CH{=}Y$ ($Y = SiH_2$, PH, S; $X = H$, CH_3, NH_2, OH, F)

Chi-Hsiang Chuang and Min-Hsiung Lien*

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, Republic of China

Received: October 16, 2003; In Final Form: January 7, 2004

We report the effects of the substituent and functional group on the tautomerizations of $H_3CC(X){=}Y$ and $H_2C(X)CH{=}Y$ ($Y = SiH_2$, PH, S; $X = H$, CH_3, NH_2, OH, F) at the G2 level of theory. In the $Y = SiH_2$ series, the enol forms ($H_2C{=}CX{-}SiH_3$) are thermodynamically more stable than their counterparts, by ca. 20−30 kcal/mol, regardless of their site of substitution. In the Y = PH and S cases, the keto forms ($H_3CC(X){=}PH$, $H_3CC(X){=}S$) are thermodynamically more stable than their counterparts by ca. 2−12 kcal/mol for the 1-substituted series, while for the 2-substituted series the enolization processes are either endothermic or exothermic, with their relative energies near 0. Combining these results with those from the previous study, the enolization is endothermic when the non-hydrogen atom in Y is more electronegative than a carbon atom and is exothermic if the former is more electropositive than the latter. Substituents with π-donating ability in the 1-substituted series increase the relative energy when Y = PH and S, but they decrease it when $Y = SiH_2$. On the other hand, in the 2-substituted series, the relative energies decrease in the sequence $H > CH_3 > F > OH > NH_2$, which is the opposite order of the increasing π-donating abilities of these substituents. The barriers to enolization in this study range from 36 to 61 kcal/mol at the G2 level of theory. The effects of the functional groups and substituents on the energy barriers are explained by interpreting Hammond's postulate in terms of the position of the transition structure along the reaction coordinate, n_T, defined by Agmon, Pearson's principle of hard and soft acids and bases, and Hammett's electron push/pull effect. By Mulliken population analysis, the electronic charge of the migrating hydrogen atom becomes gradually negative, which indicates the tautomeric interconversion is as an $H^{\delta-}$ transfer (or a hydride transfer). This is in contrast with that of the analogous process that occurs for compounds of the second period (Y = O, NH, and CH_2).

Introduction

Tautomerization that relates to the transfer of π electrons between a heteronuclear double bond and a C═C double bond is a very important process in organic chemistry and biochemistry. The most common examples are keto−enol,[1] imine−enamine,[2] oxime−nitroso,[3] hydrazo−azo,[4] and phenol−keto[5] isomerizations. In many organic reactions, e.g., electrophilic substitutions of carbonyl compounds, oxy-Cope, Conia, and Carrol rearrangements, and retro Diels−Alder reactions, enolization processes are rate-determining steps. Erlenmeyer[6] reported in 1881 that, upon their formation, vinyl alcohols rearrange to form aldehydes and ketones. Since then, various tautomerizations have been studied extensively both experimentally and theoretically.[7] Fewer studies, however, have been carried out on tautomeric processes involving atoms of the third row of the periodic table (e.g., Si, P, and S). The central position of silicon in the periodic table, at the borderline between organic and inorganic chemistry on one hand and between metallic and nonmetallic elements on the other, results in the manifold, and often unique, chemical behavior of its compounds. Although organic silicon reagents are very important in organic reactions, for example, trialkylsilyl groups are used commonly as protecting groups in the synthesis of α-hydroperoxy carbonyl compounds,[8] there are relatively fewer studies concerning the C═Si double bond.[9] Maier[10] has used ab initio calculations to investigate the reaction of silicon and methyl alcohol that produces silenes ($H_2C{=}SiHOH$, $H_2Si{=}CHOH$); Leigh[11] has studied the effect of substituents on the activity of the C═Si double bond; and Nagase et al.,[12] Gordon et al.,[13] and Olbrich[14] have calculated the energy barriers for silylene−silene and silylsilylene−disilene isomerizations. Phosphorus is ubiquitous in our world, with diverse roles ranging from being a key element in the genetic blueprint[15] to being an essential element in agriculture. Species having a double bond between a 2-coordinate phosphorus atom and an O, S, N, or C atom are very important in organic and inorganic reactions. Neilson and Angelov have studied the latter two of these species.[16] The heteroatomic double bond in these 2-coordinate phosphines is highly polar in nature; the partial positive charge on the phosphorus atom makes it an electrophilic center. The sp^2-hybridized phosphorus atom, however, also carries a lone pair of electrons and exhibits nucleophilic character, which is important for some metal complexation, addition, and cycloaddition reactions. Sulfur is a common element in numerous industrial, agricultural, and medicinal compounds.[17] The compounds and chemistry of sulfur have been researched very extensively.[18] Hall et al. have investigated the Diels−Alder reactions of thioaldehydes and thioketones.[19] Castro has studied the reaction mechanisms and kinetics of thioketones.[20] It has been noted in the study of thione−enethiol tautomerization that thials and thiones having α-hydrogen atoms can form the

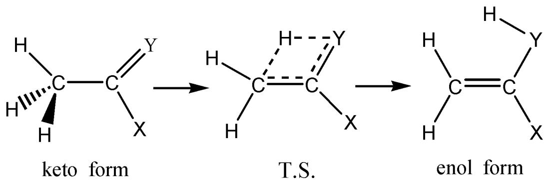
---

* Author to whom correspondence may be addressed. E-mail: g8851143@mail.nchu.edu.tw.

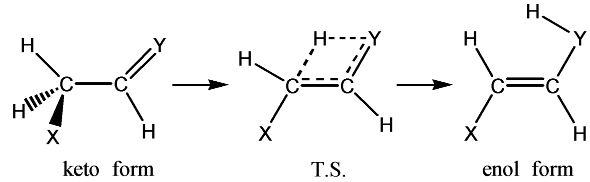
10.1021/jp0371332 CCC: $27.50

SCHEME 1

(a) 1-substituted series



(b) 2-substituted series



$Y = SiH_2$, PH, S; $X = H$, CH_3, NH_2, OH, F

corresponding enethiols and that this process is greatly favored relative to the enolization of carbonyl compounds. Thus, upon generating a thioketone, quite often a rapid transition occurs from the thiocarbonyl tautomer into the enethiol form. This phenomenon is true for 1,3-diphenyl-2-propanethione, cyclopentanethione,[21] and for cyclopentanethione.

Previously, we reported the results of our studies on substituent effects in 1- and 2-substituted keto−enol[22] and 2-substituted imine−enamine[23] tautomerizations. Recently, we reported the effects of substituents and functional groups in the isomerizations of 1- and 2-substituted propenes, acetaldimines, and aldehydes.[24] Our results at the G2 level of theory have demonstrated the following features: (1) Among the six tautomeric series investigated, the keto forms are thermodynamically more stable than the enol forms, except for the 1-substituted propene−propene ($Y = CH_2$) series, in which the enol and keto forms represent the same species, and for the 2-substituted propene−propene series, in which the enol forms are lower in energy than the keto forms. (2) In the 1-substituted series, π-donating substituents increase the relative energies (enol form vs keto form) by stabilizing the keto form over the enol form; the opposite is true in the 2-substituted series. (3) In both the 1- and 2-substituted series, the influence of the functional group Y increases the energy barriers in the sequence $NH_2 < O < CH_2$. In the 2-substituted series, substitution by X lowers the energy barrier, but conversely, in the 1-substituted series, the presence of the substituent lowers the energy barrier only when $Y = CH_2$; when Y = NH and O, the energy barrier increases in the order $NH_2 < CH_3 < H < OH < F$. (4) The computed relative energies increase upon increasing the electronegativity of the non-hydrogen atom in the functional group; a very good linear correlation exists between these two sets of numbers. We predict that enolization is highly endothermic when the non-hydrogen atom in the Y unit is more electronegative than is a carbon atom and is exothermic if the former is more electropositive than is the latter.

To add further weight to our forecast and to increase the completeness of our survey of the effects of functional groups and substituents on the relative energies and energy barriers in tautomerization processes, we have extended, and now present, our studies on the corresponding series of compounds in the third row of the periodic table (Scheme 1). We define the forms $CH{-}C{=}SiH_2$, $CH{-}C{=}PH$, and $CH{-}C{=}S$ as keto forms and their tautomeric counterparts, $C{=}C{-}SiH_3$, $C{=}C{-}PH_2$, and $C{=}C{-}SH$, as enol structures (forms).

Computational Methods

Ab initio molecular orbital and density functional theory (DFT) calculations were carried out using Gaussian 98 packages. All of the geometric structures of the stationary points in the potential-energy surface were optimized at the HF/6-31G**,[25] MP2(full)/6-31G* (to be used for the G2 calculations), and B3LYP/6-31G** levels of theory. Calculations of the harmonic vibrational frequencies were performed to characterize the local minima and saddle points and furnish the zero-point vibrational energies. Calculations of intrinsic reaction coordinates (IRC)[26] were performed at the HF/6-31G** level of theory to establish the connection of the transition structures and the corresponding local minima along the reaction pathways. The natural bond orbital (NBO)[27] technique was used to analyze the natural bond population, stabilization energy, and the quantity of charge transfer. To examine the nature of the local charge flow ($H^{\delta+}$ or $H^{\delta-}$ transfer) within a species along the reaction path and, thus, to identify the mode of hydrogen atom migration, we applied IRC calculations to obtain the atomic charges from the Mulliken population analysis (MPA) using the HF/6-31G** structures.

Results and Discussion

Similar trends exist between the geometries, relative energies, and energy barriers calculated at the various levels of theory in this study. Thus, unless otherwise stated, we report only the results of calculations at the G2 level of theory.

A. Geometric Structures. Figure 1 depicts the optimized structures of the stationary points on the potential-energy surface for the parent thioketone structure (Y = S, X = H) at the MP2(full)/6-31G* level.[28] All the local minima of the keto and enol forms have either C_s or C_1 symmetry, while the transition structures all have the same C_1 symmetry with the migrating hydrogen atom (H4) being somewhat out of the plane of the C1−C2−Y3 unit in a slightly distorted four-membered ring structure.

B. Relative Energies. The relative energies of the enol forms with respect to their keto forms are listed in Table 1 and illustrated in Figure 2. These results indicate the following features: (1) In the $Y = SiH_2$ series, the enol forms ($H_2C{=}CX{-}SiH_3$) are thermodynamically more stable than their counterparts by ca. 20−30 kcal/mol ($E_r < 0$), regardless of the site of substitution. (2) In the 1-substituted series, the opposite is true for Y = PH and S, where the keto forms are lower in energy by ca. 2−12 kcal/mol ($E_r > 0$). (3) In the 2-substituted series, the thermodynamic stabilities of the enol forms are higher than those of their counterparts for Y = PH, except when X = H; in the Y = S series, the stabilities of the enol forms and the keto forms depend on the electron-donating ability of the substituents: π-donating substituents, such as NH_2 and OH, are more stabilizing to the enol forms than to their counterparts. In this series, the enolizations are either endothermic or exothermic, with relative energies almost near 0.

In short, the relative energies increase upon increasing the electronegativity of the functional group and the effects of the substituents depend on the site of substitution. In the 1-substituted Y = PH and S series, the substituents are more stabilizing in the keto form, which results in an increase in their relative energies, while the opposite is true for all of the 2-substituted series and the 1-substituted series when $Y = SiH_2$.

B.1. The Effects of the Functional Groups. As we see in Table 1, the correlation coefficient *R* of the linear regression ranges from 0.8250 to 0.9359 for the six tautomeric series in this study and from 0.9863 to 0.9996 for the analogous series

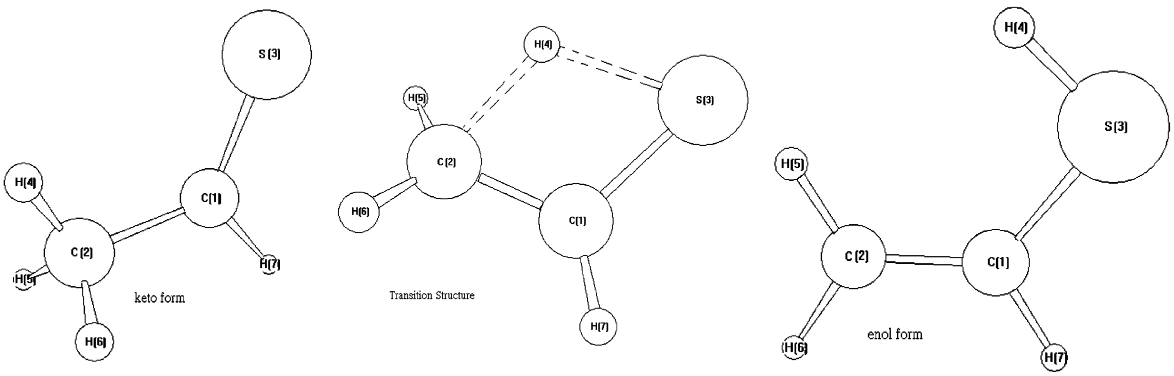


Figure 1. The optimized structure of keto form, transition structure, and enol form for Y = S, X = H at the MP2(full)/6-31G* level of theory.

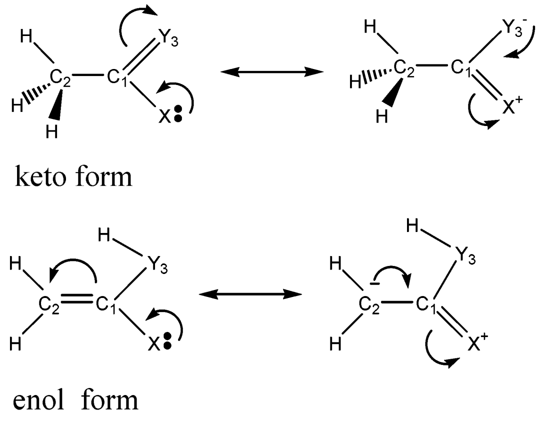
TABLE 1: Relative Energies[a] (kcal/mol) and the Correlation Coefficient (*R*) of Linear Correlation between the Relative Energies and the Electronegativity (Pauling's Scale) of the Non-Hydrogen Atoms in the Functional Groups at the G2 Level of Theory

X/Y	SiH_2(1)[b]	P(1)	S(1)	*R*	SiH_2(2)	P(2)	S(2)	*R*
H	−18.59	2.41	2.56	0.8250	−18.59	2.41	2.56	0.8250
CH_3	−19.31	2.80	4.29	0.8528	−21.81	−0.51	0.12	0.8361
NH_2	−19.03	8.03	17.20	0.9359	−29.87	−5.87	−5.26	0.8342
OH	−22.37	6.84	11.84	0.8915	−26.98	−4.98	−2.36	0.8733
F	−21.98	4.00	11.97	0.9289	−22.26	−1.57	0.70	0.8698

X/Y	CH_2(1)[c]	NH(1)	O(1)	*R*	CH_2(2)	NH(2)	O(2)	*R*
H	0.00	4.22	11.90	0.9863	0.00	4.22	11.90	0.9863
CH_3	0.00	5.03	13.58	0.9890	−3.02	2.40	9.69	0.9964
NH_2	0.00	9.79	25.32	0.9915	−7.98	2.15	9.62	0.9962
OH	0.00	10.42	23.91	0.9973	−6.39	2.31	10.23	0.9996
F	0.00	12.17	26.65	0.9988	−3.23	3.91	12.03	0.9993

[a] The relative energy of the enol form with respect to the keto form. [b] The number in the bracket indicates the site of substitution. [c] Data from ref 24.

SCHEME 2



of the second period (Y = CH_2, NH, and O). Although the values of *R* are less than those calculated for the compounds of the second period elements, there is still a good linear correlation between the relative energies of $H_3CC(X){=}Y$ and the electronegativity (Pauling scale) of the non-hydrogen atom in Y. The combined correlation coefficients *R* of the linear regression range from 0.8008 to 0.8951. In both the 1- and 2-substituted series, increasing the electronegativity of the non-hydrogen atom in Y leads to an increase in the relative energy as a result of the bond energy and resonance effects of the polar heteroatomic double bond.

In the 1-substituted series, as indicated in Scheme 2, the substituent X, which is bonded directly to the C=Y double bond in the keto form and the C=C double bond in the enol form, has a significant influence on the stabilities of the tautomers. The magnitude of this influence, which is expressed quantitatively in Table 2 in terms of the stabilization energies (E_s) and the quantity of charge transfer (QCT), is a consequence of the π-accepting abilities of the C=Y and C=C double bonds.

In the case of Y = SiH_2, the fact that silicon is more electropositive than is carbon prohibits the formation of a $C^{\delta+}{=}Si^{\delta-}$ species so that the C=C double bond tends to withdraw more electron charge from the lone pair electrons in the substituent group (LP_X) to the antibonding orbital of the C=C double bond (C=C*). This situation results in the enol forms being more stable than the keto forms. In the series Y = PH and S, although the electronegativities of P (2.1)[29] and S (2.5) atoms are lower than that of a C atom (2.5), the resonance effect of the substituents favors the keto forms. Since they belong to the third row of the periodic table, P and S atoms have large covalent radii that result in large bond lengths and dipole moments for their C=Y double bonds; this feature gives P and S atoms the ability to accept π electrons from π-donating substituents through conjugation or negative conjugation. We see from Table 2 that in the Y = SiH_2 series the stabilization energies and QCTs of $LP_X \rightarrow$ C=C* are greater than those of $LP_X \rightarrow$ C=Si*; in contrast, in the series Y = PH and S, the latter are greater than the former. The relative energies of the series of compounds in this study are apparently much lower than those of the corresponding series (Y = CH_2, NH, and O) in our previous study. This phenomenon occurs because of the bond-energy effect. The higher electronegativities of C, N, and O atoms (relative to Si, P, and S atoms, respectively) cause the C=Y double bonds of the keto forms to be stronger (relative to C=Si, C=P, and C=S bonds, respectively) and raise their relative energies. Lacking the bond-energy effect, the relative energy of the enol form with respect to the keto form in this study is smaller than that calculated for compounds containing the second-row elements.

In the 2-substituted series, the substituents X are bonded to C2, which is part of the C=C double bond in the enol form, but in the keto form they are not attached to the double bond. The data obtained from the NBO calculations indicate that the stabilization of the enol structure results from conjugation (hyperconjugation for X = CH_3) between the lone pair of electrons of the functional groups and substituent groups. The keto form on the other hand is stabilized mainly by the negative hyperconjugation effect between the functional group C=Y and the C2—C1 and C1—H bonds (Scheme 3).

Table 3 indicates that both the stabilization energy and the QCT are larger in the enol form than they are in the keto counterpart, which indicates that the delocalization effect favors the enol form. This situation results in the relative energy being

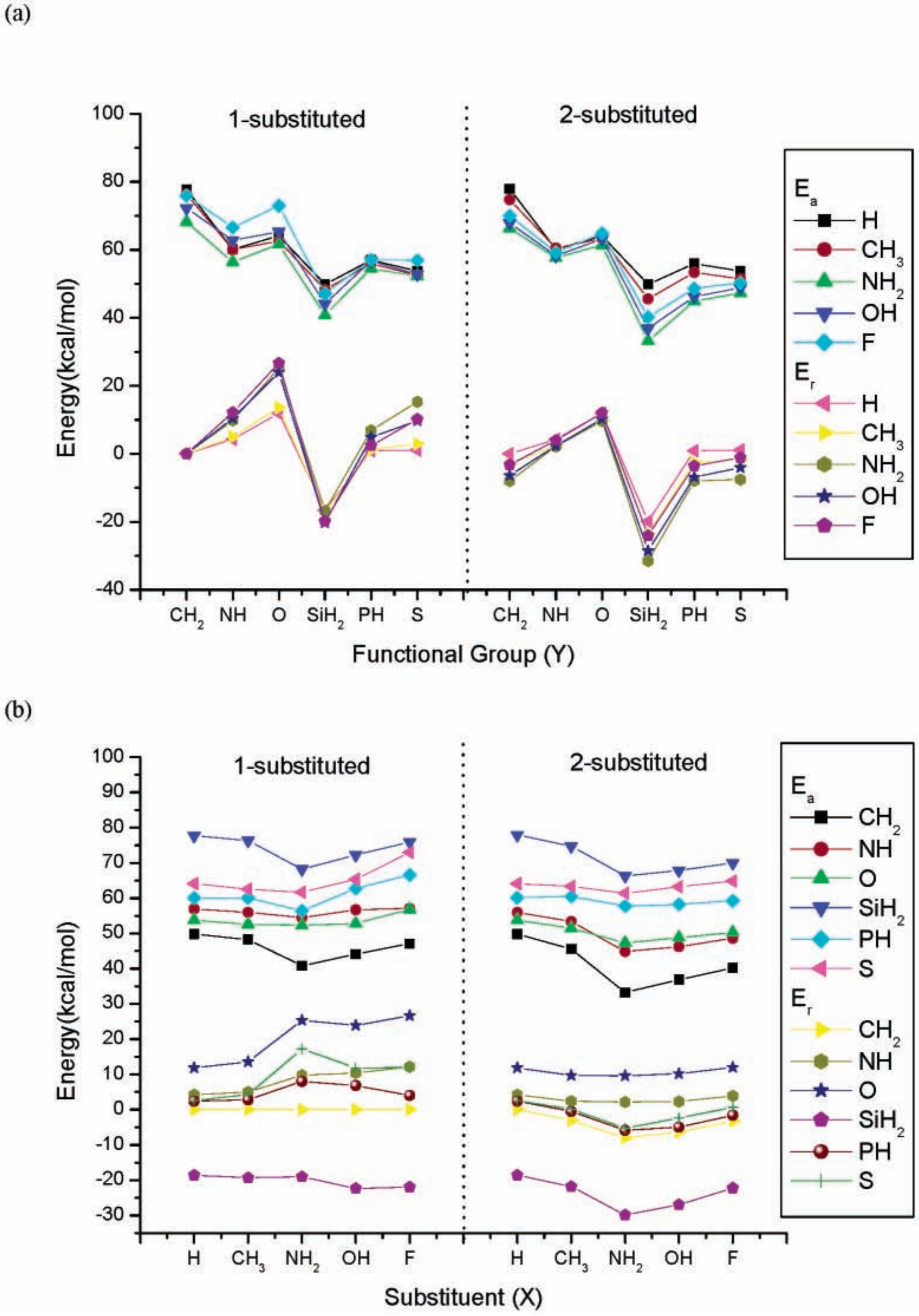


Figure 2. The effects of the functional groups (a) and substituents (b) on the energy barriers of the "enolization" and the relative energies of the enol form with respect to the keto form at G2 level of theory.

TABLE 2: Stabilization Energies and QCT of LpX → C=Y* in the Keto Forms and LpX → C=C* in the Enol Forms of Compounds in the 1-Substituted Series

	keto form						enol form					
	SiH_2		PH		S		SiH_2		PH		S	
X/Y	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT
H	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000
CH_3	5.75	0.008	15.74	0.027	18.14	0.032	12.14	0.018	12.61	0.019	13.44	0.020
NH_2	3.32	0.004	94.47	0.300	116.26	0.375	36.02	0.081	35.03	0.076	29.03	0.053
OH	28.44	0.063	70.79	0.168	80.51	0.199	47.76	0.096	48.66	0.097	51.26	0.103
F	20.92	0.032	45.74	0.088	56.91	0.112	34.29	0.058	35.42	0.059	37.38	0.062

either negative or almost near zero, which is very different from the corresponding results obtained for the compounds featuring elements of the second row in the periodic table. In the latter series, although the delocalization effects are more stabilizing

TABLE 3: Stabilization Energies and QCT of the Local Minima (Keto and Enol Forms) in the 2-Substituted Series

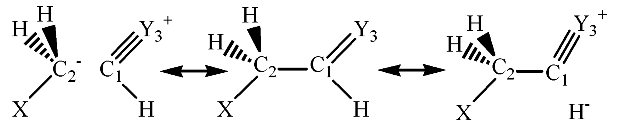
Enol Form

	S						PH						SiH_2					
	$LP_X \rightarrow C{=}C^*$		$LP_Y \rightarrow C{=}C^*$		sum		$LP_X \rightarrow C{=}C^*$		$LP_Y \rightarrow C{=}C^*$		sum		$LP_X \rightarrow C{=}C^*$		$LP_Y \rightarrow C{=}C^*$		sum	
X\Y	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT
H	0.00	0.000	31.99	0.079	31.99	0.079	0.00	0.000	12.50	0.021	12.50	0.021	0.00	0.000	4.22	0.007	4.22	0.007
CH_3	13.18	0.020	29.28	0.070	42.46	0.090	13.80	0.021	11.92	0.020	25.72	0.040	14.18	0.021	4.08	0.007	18.26	0.028
NH_2	17.54	0.022	30.27	0.073	47.81	0.080	47.87	0.114	9.73	0.015	57.60	0.129	57.30	0.131	3.78	0.006	61.08	0.137
OH	54.93	0.109	10.03	0.014	64.96	0.124	42.66	0.092	10.14	0.016	52.80	0.108	50.60	0.103	3.93	0.007	54.53	0.110
F	36.12	0.060	28.82	0.070	64.94	0.130	38.22	0.063	10.76	0.004	48.98	0.068	39.80	0.066	4.12	0.007	43.92	0.073

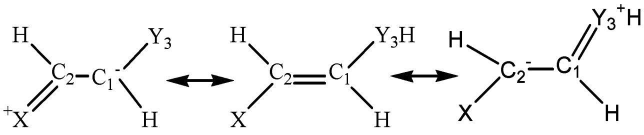
Keto Form

	S						PH						SiH_2					
	$LP_Y \rightarrow C{-}C^*$		$LP_Y \rightarrow C{-}H^*$		sum		$LP_Y \rightarrow C{-}H^*$		$LP_Y \rightarrow C{-}C^*$		sum		$LP_Y \rightarrow C{-}C^*$		$LP_Y \rightarrow C{-}H^*$		sum	
X\Y	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT	E_s	QCT
H	16.76	0.025	13.49	0.020	30.25	0.045	0	0	6.78	0.008	6.78	0.008	2.63	0.003	1.64	0.002	4.27	0.005
CH_3	16.54	0.025	13.69	0.020	30.23	0.045	0	0	6.88	0.008	6.88	0.008	2.61	0.003	1.68	0.002	4.29	0.005
NH_2	16.76	0.026	13.49	0.020	30.25	0.045	0	0	7.06	0.008	7.06	0.008	2.54	0.003	1.75	0.002	4.29	0.005
OH	17.09	0.027	13.28	0.019	30.37	0.046	0	0	7.11	0.008	7.11	0.008	2.51	0.003	1.73	0.002	4.24	0.005
F	17.33	0.027	13.54	0.020	30.87	0.047	0	0	7.21	0.008	7.21	0.008	2.49	0.003	1.77	0.002	4.26	0.005

SCHEME 3



negative hyperconjugation of keto form



conjugation of enol form

in the enol form than they are in the keto congener, the C1═Y3 bond energy of the keto form is 20−30[30] kcal/mol larger than that of the C1═C2 bond in the enol form. This result demonstrates that the effect of the bond energy, which favors the keto form, is more dominant than the effect of delocalization. Compared with the C, N, and O atoms, the corresponding atoms in this study, Si, P, and S, have smaller electronegativities, larger valence radii, and more d character in the Y atom of the C═Y double bond. These characteristics cause the bond-energy property, which favors the keto form, to take a lesser role relative to the effect of delocalization. As Table 1 displays, the tautomers in the enol form are lower in energy than their counterparts, except for the series where Y = PH, X = H and Y = S, X = H, CH_3, and F.

By combination of the results of our two studies, the effect of functional group C═Y on lowering relative energies increases in the sequence O < S < NH < PH < CH_2 < SiH_2 for the 1-substituted series, but in the 2-substituted series, they are in the order O < NH < S < PH < CH_2 < SiH_2. From these observations, we suggest that the tautomers having enol forms become gradually more stable than their counterparts upon increasing the atomic number of the element Y, of the same group in the periodic table, because of decreases in the strengths of the C═Y double bonds.

B.2. The Effects of the Substituents. Table 1 and Figure 2 exhibit that substituents having π-donating ability in the 1-substituted series increase the relative energy (the enol form with respect to the keto form) when Y = PH and S, but they decrease the relative energy if Y = SiH_2. On the other hand, in the 2-substituted series, the relative energies decrease in the sequence H > CH_3 > F > OH > NH_2, which is the opposite order as the increasing π-donating abilities of these substituents.

In the 1-substituted series, the π-donating substituents stabilize the enol forms and decrease the relative energy when Y = SiH_2, but the abatement of the relative energy is not proportional to the π-donating ability of the substituents. Because of its low electronegativity, the Si atom in the C═Si double bond prefers carrying a positive charge; electron-withdrawing substituents decrease the relative energy by stabilizing the keto tautomers. The linear correlation coefficient (*R*) between the relative energies and the group electronegativities (Pauling scale) of the substituents is 0.8175. Both electron-donating and electron-withdrawing abilities of substituents cause the effects of the substituent on the relative energies to follow the sequence OH < F < CH_3 < NH_2 < H. When Y = PH, the substituents donate more π electrons to the C═Y double bond in the keto tautomers than to the C═C double bond in their counterparts, and this phenomenon causes the relative energies to increase in the order H < CH_3 < F < OH < NH_2, which is also the sequence of their π-electron-donating character. For the case of Y = S, the S atom delocalizes more of its lone pair of electrons to the highly electronegative F atom than to the OH substituent, which results in the effects of the substituents on the relative energies to follow the order H < CH_3 < OH < F < NH_2.

In the 2-substituted series, the substituents stabilize the enol forms over the keto forms by delocalizing the π electrons of the C═C double bonds. The magnitude of the influence that the substituents exert on the stabilization energy and QCT follows the order H < CH_3 < F < OH < NH_2, which, again, is the sequence of their π-donating ability. This effect leads the relative energies being in the order H > CH_3 > F > OH > NH_2.

C. Energy Barrier. Table 4 lists, and Figure 2 illustrates, the energy barriers calculated for converting the keto forms to the enol forms via intramolecular 1,3 hydrogen-atom shifts for the six tautomeric processes. The barriers to enolization, ranging from 36 to 61 kcal/mol, are rather high but are considerably lower than those computed for their analogues with second row atoms.

TABLE 4: Energy Barriers and Values of n_T Calculated at the G2 Level of Theory

	Si(1)[a]		P(1)		S(1)		Si(2)		P(2)		S(2)	
X/Y	E_a	n_T	E_a	n_T	E_a	n_T	E_a	n_T	E_a	n_T	E_a	n_T
H	53.11	0.4167	60.87	0.4961	58.11	0.5157	53.11	0.4167	60.87	0.4962	58.11	0.5157
CH_3	51.83	0.4114	60.13	0.4975	57.04	0.5242	49.19	0.4006	57.86	0.4289	56.50	0.5062
NH_2	44.26	0.4171	58.17	0.5252	56.66	0.5893	36.31	0.3561	49.27	0.4289	52.15	0.5053
OH	47.19	0.3917	60.79	0.5118	57.08	0.5494	39.71	0.3745	50.27	0.4289	53.09	0.4986
F	50.57	0.4018	60.96	0.4989	61.29	0.5449	43.47	0.3938	52.89	0.4289	55.34	0.5148

[a] The number in the parentheses indicates the site of substitution.

Since the structure of a transition state reflects, in part, that of the reactants and products, analyzing the character of a transition structure is conducive to understanding the trends that result in variations in energy barriers. The Hammond postulate[31] is a useful tool for relating a transition structure to the structure of its reactants and products. It follows from Hammond's statement that there are three possible situations in a potential-energy surface. The first defines a highly exothermic step having a low energy barrier; the transition state will resemble the reactant structurally for they are close in energy and, therefore, are interconverted through only a small structural change. This phenomenon implies only a small displacement along the reaction coordinate toward the product. The second case defines an endothermic step in which the energy of the transition state is closer to that of product, and so is the structure. The third case characterizes a process in which the transition state is much higher in energy than either the reactant or the product; in this situation, neither the reactant nor the product is similar in structure to the transition state. By comparison of our present study with our earlier one, and noting that since the Y = SiH_2 and Y = CH_2 series are highly exothermic with the liberation of heat in the former being ca. 20 kcal/mol higher than the latter, the energy barriers of the latter are lower than those of the former. In the highly endothermic cases, namely, the 1-substituted Y = S and Y = O series, the absorptions of heat in the former are less than those of the latter by ca. 10 kcal/mol, so the energy barriers to enolization of the latter are lower than those of the former. The relative energies of the 1-substituted Y = PH series are similar to those of the 1-substituted Y = NH series, and it is true that the energy barriers follow the same trends. These observations imply that the tautomerizations, which are a competition between a homoatomic C═C double bond and a hetroatomic C═Y double bond, are in accord with the Hammond postulate.

The Hammond postulate can be interpreted quantitatively in terms of the position of the transition structure along the reaction coordinate, n_T, defined by Agmon[32]

$$n_T = \frac{1}{2 - (\Delta G^0/\Delta G^{\ddagger})}$$

where $\Delta G°$ is the difference in Gibbs free energy between the enol and keto forms and $\Delta G^{\ddagger}$ is the Gibbs free energy of activation for converting the keto form into the enol form. The magnitude of n_T values, which are indicative of the degree of similarity between the transition structure and the product, are 0, 0.5, and 1 for the reactant (the keto form), transition state, and product (the enol form), respectively. Table 4 lists the computed values of n_T for the six tautomeric processes examined in this study. In the 1-substituted series, the values of n_T are below 0.5 for Y = SiH_2. This result means that the transition structures resemble the keto forms, and thus, there is a lower barrier to enolization in the Y = SiH_2 series. The values of n_T, however, are greater than 0.5 when Y = PH and S, and so the late transition structure resembles the enol form more than its tautomeric counterpart. This phenomenon leads to relatively higher energies for the transition structures, which results in higher barriers to enolization than are found in the Y = PH and S series. In the 2-substituted series, with Y = SiH_2, results are obtained as they were for the 1-substituted series. The values of n_T are below 0.5 for the Y = PH series, with the exception of X = H, and above 0.5 for the Y = S series, with the exception of X = NH_2 and OH, which are the most strongly π-donating substituents. Because the relative energies in these two series are almost near 0, which suggests the third case described above for the Hammond postulate ($n_T \sim 0.5$), the transition states are much higher in energy than either the reactants or the products, and the barriers to enolization are higher than that in Y═SiH_2 series.

C.1. The Effects of the Functional Groups. In our previous study, for a given substituent, the energy barries for converting the keto form to the enol form, with respect to the functional groups C═Y, follow the order CH_2 > O > NH for both the 1-and 2-substituted series. In this present study, however, the energy barriers increase in the sequence SiH_2 < S < PH (except that in the 2-substituted series the order is SiH_2 < PH < S when X = NH_2, OH, and F). Thus, the trends in the energy barriers to enolization in these two studies are different. In the following section we explain this observation by MPA and Pearson's principle of hard and soft acids and bases (HSAB).

C.1.1. MPA. The rate of the 1,3 shift of a hydrogen atom during tautomerizations depends on the energy of the C2—H4 bond of the migrating hydrogen atom (H4) and the pulling and pushing ability of the C1═Y3 functional group. Furthermore, the "pull and push" effect of the C1═Y3 bond hinges on the electronegativity of the non-hydrogen atom in Y (the σ-withdrawing ability) and the π-donating ability of the C═Y double bond. Figure 3 illustrates profiles of the trends in the change of the charges on relevant atoms in the molecule by MPA in IRC calculations. Here, we discuss the results only for X = H.[33] As we see in Figure 3a, the electronic charge of the non-hydrogen atom in Y (Si and P) is positive while that of C1 is negative in the series Y = SiH_2 and PH. In this series Y = S, although the electronic charge of S3 is negative, it is positive relative to that of C1. This interpretation is in agreement with the relevant experimental report on thioketones[34] and the theoretical calculations on thioformaldehyde.[18e,35] The greater the decrease in electronegativity of the non-hydrogen atom in Y relative to that of C1, the greater is the delocalization of the π electron in C═Y to $C^{\delta-}$═$Y^{\delta+}$; in the meantime, the electronic charge of the migrating hydrogen atom becomes gradually negative. We denote this tautomeric interconversion of the migrating hydrogen atom with partial negative charge as an $H^{\delta-}$ transfer (or a hydride transfer). On the other hand, Figure 3b displays that in our previous study the mode of hydrogen atom migration is that of a partial buildup of positive charge, with $C^{\delta+}$═$Y^{\delta-}$, which we call an $H^{\delta+}$ transfer (or proton transfer) when the non-hydrogen atom in Y is C, N, and O. In the case of $H^{\delta-}$ transfer, the lower electronegativity of the non-hydrogen atom

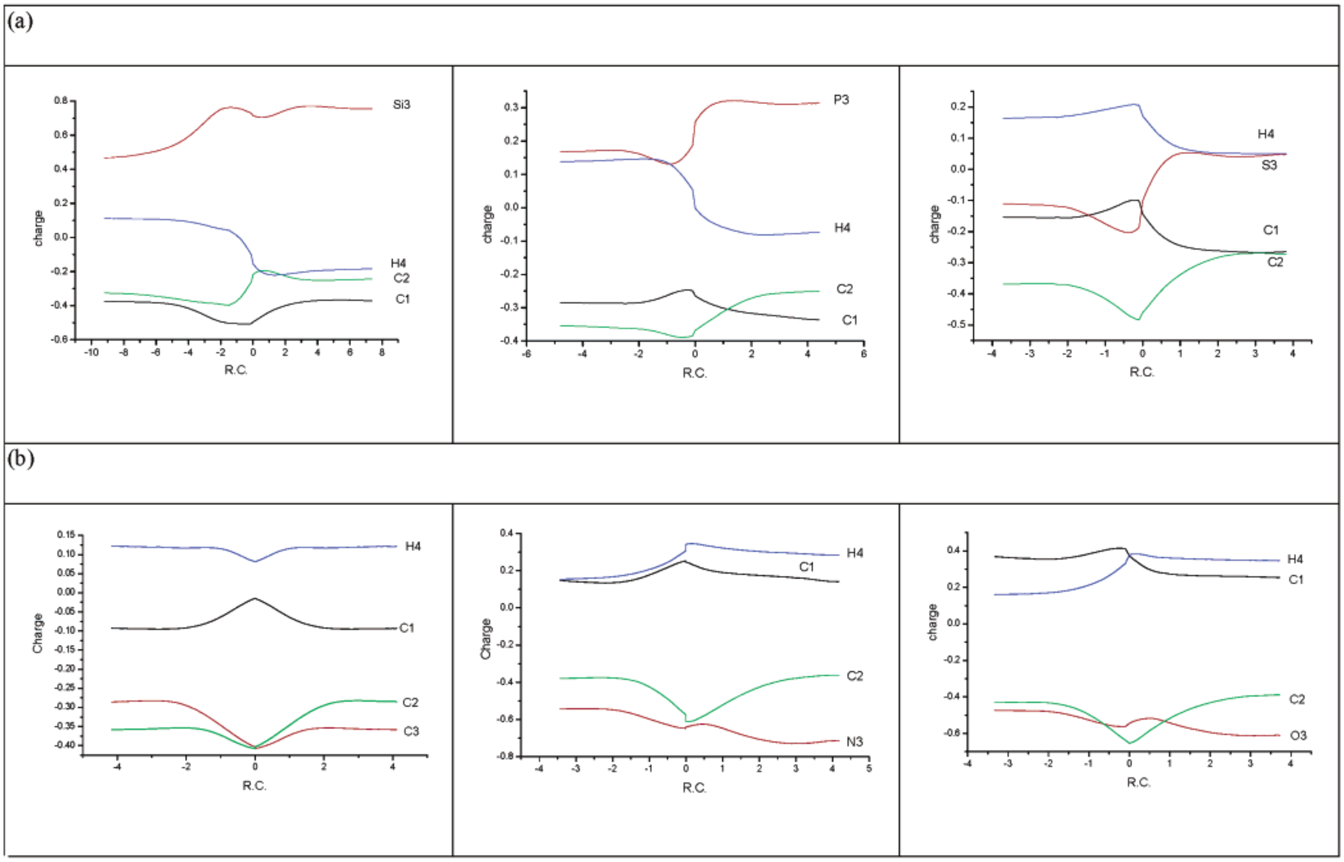
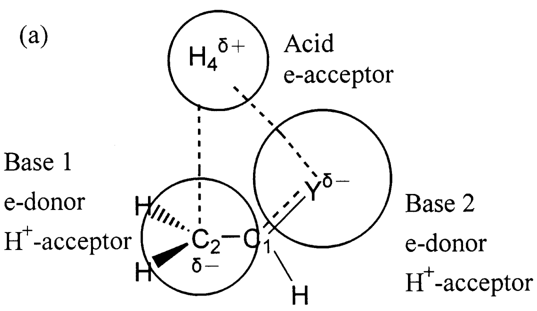


Figure 3. Profiles of the charge of the main atoms at the HF/6-31G** level of theory. (a) Data from this study (Y = SiH_2, PH, S; X = H); $H^{\delta-}$ transfer. (b) Data from ref 24 (Y = CH_2, PH, O; X = H); $H^{\delta+}$ transfer. The keto form, transition structure, and enol form are on the left-hand side, in the center, and on the right-hand side of the reaction coordinate, respectively.

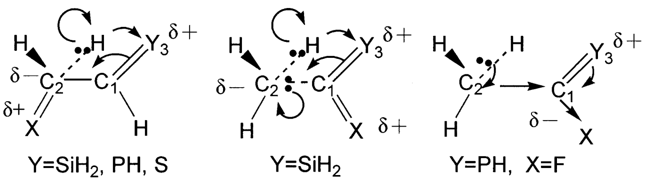
CHART 1



in Y causes C=Y to have a $C^{\delta-}$=$Y^{\delta+}$ structure, and acts as an electron acceptor to accept the negatively charged migrating hydrogen atom (H4) and, therefore, reduces the energy barrier. In contrast, in the case of $H^{\delta+}$ transfer, the higher electronegativity of the non-hydrogen atom in Y decreases the energy barrier. Because the smallest electronegativity in the series is that of the Si atom (1.8 on the Pauling scale), the energy barrier of the Y = Si compound is the lowest in the studied $H^{\delta-}$ transfer processes, but for the $H^{\delta+}$ transfer processes, in which the C atom has the smallest electronegativity of the series, the energy barrier is the highest.

C.1.2. Pearson's Principle of Hard and Soft Acids and Bases.[36] As mentioned in the preceding section, polarizability is a fundamental atomic characteristic, which is closely related to electronegativity, that describes the response of an atom's electrons to nearby charges. Here, another important atomic property closely related to electronegativity is "hardness" (η). Highly electronegative atoms tend to be hard, and less electronegative atoms are relatively softer. According to Pearson's concept of chemical hardness and softness, the hardness of atoms increases in the order C (5.0) < O (6.1) < N (7.3);[37] H^+ (∞) is a very hard acid. As presented in Chart 1a for the transition structure in the $H^{\delta+}$-transfer series, the migrating hydrogen atom having partial positive charge is a local acid and the atoms C2 and Y3 having partial negative charge are local bases. Since a hard acid prefers a hard base (i.e., the HSAB principle), the trend in increasing the competition for the acid between these two basic sites occurs in the sequence C < O < N. This situation results in the energy barriers to enolization of C=Y compounds decreasing in the opposite order: CH_2 > O > NH. Chart 4b depicts the transition structure for the $H^{\delta-}$-transfer series in this study. The hardness of the non-hydrogen atom in Y increases in the order Si (3.4) < S (4.1) < P (4.9); the softness ($1/\eta$) increases in the inverse order. The hardness of the hydride ion (H^-) is low (η = 6.8) because of its low electronegativity; in other words, it is a soft base. Again, according to the HSAB principle, soft bases prefer soft acids, with the ability of the Y group accepting the migrating hydride ion increasing in the order

CHART 2



(a) (b) (c)

$P < S < Si$. In contrast, the order of the decreasing energy barrier is $PH > S > SiH_2$.

C.2. The Effects of the Substituents. The results obtained from G2 calculations (Table 4) indicate that in the 1-substituted series all the substituents we studied lower the energy barriers when $Y = SiH_2$; in the cases $Y = PH$ and $Y = S$, with the exception of $X = F$, the substituents also lower the energy barriers. All substituents we studied in the 2-substituted series lower the energy barriers. The energy barriers of the "enolization" when $Y = SiH_2$ in the 1-substituted series and for the various functional groups in 2-substituted series all follow the following sequence for X: $H > CH_3 > F > OH > NH_2$. As noted above, the effect of the substituent has greater impact on the enol form than on the keto form, and the transition structures all have some enol content. Therefore, the substituents that stabilize the enol form over the keto form also stabilize the transition structure and, therefore, they lower the energy barrier. As already indicated in the previous discussion, the ability of the substituents to stabilize the enol form increases in the order $H < CH_3 < F < OH < NH_2$, which is also the sequence of the lowering energy barriers. In the 1-substituted tautomeric series with $Y = PH$, substitution by the electron-withdrawing F atom, which pulls electron density from the C2−H4 bond, leads to a higher energy barrier, and hence, the order of the energy barriers with respect to X is $NH_2 < CH_3 < OH < H < F$.

We have examined the correlation between the energy barrier and the resonance effect of the substituent using the empirical equation

$$\Delta G^{\ddagger} = A + B\sigma_R$$

where $\Delta G^{\ddagger}$ is the energy barrier and σ_R is the Hammett substituent resonance parameter. A very good linear correlation exists between the energy barriers and resonance effect of the substituents. The correlation coefficient (R) of the linear regression ranges from 0.9739 to 0.9940 for the 1-substituted series when $Y = SiH_2$ and all cases in the 2-substituted series (1-substituted series for $Y = SiH_2$, 0.9793; 2-substituted series for $Y = SiH_2$, 0.9940; for $Y = PH$, 0.9739; for $Y = S$, 0.9867). As we see in Chart 2a for the 2-substituted series in which the substituent X is bonded to C2, electron-donating substituents, such as NH_2, OH, F, and CH_3, tend to increase the electron density of the C2−H4 bond and favor the transfer of a partially negatively charged H4 atom to the partially positively charged non-hydrogen atom in Y, which is a situation that, therefore, decreases the energy barrier. Chart 2b illustrates that for the 1-substituted series having $Y = SiH_2$, in which the substituent X is bonded to C1, electron-donating substituents donate electron density to both the C1═Si double bond through conjugation, which is detrimental to $H^{\delta-}$ transfer, and to C1 through negative conjugation, which decreases the electronegativity of C1 and assists H4 in leaving with negative charge. Because of the low electronegativity of Si, the latter dominates the former and a lower energy barrier ensues. Chart 2c indicates that, for the 1-substituted series having $Y = PH$, the strongly electron-withdrawing F atom draws electron density toward the C2 atom of the C2−C1 bond through an electron-induction effect. This phenomenon increases the electronegativity of C2 and inhibits H4 from migrating with partial negative charge, which is a situation that, therefore, raises the energy barrier of the process. In this series, the correlation coefficient R of the linear regression is very small, 0.5874, but it improves to 0.9924 when the strongly electron-withdrawing F atom is excluded.

Conclusion

On the basis of this theoretical study, we reach the following conclusions:

(1) The tautomeric interconversions examined in this paper are processes in which the homonuclear C═C and heteronuclear C═Y double bonds compete for π electrons. The abilities of these double bonds to accept π electrons depend on the electronegativity of the non-hydrogen atom of the functional group Y, the properties of the substituents, and the site of substitution.

(2) The computed relative energies (enol form vs keto form) increase upon increasing the electronegativity of the functional group. There is a very good linear correlation between the relative energies and the electronegativity (Pauling scale) of the non-hydrogen atom in the functional group. The enolization is highly endothermic when the non-hydrogen atom in Y (e.g., an O atom) is more electronegative than is a carbon atom and is exothermic if the former (e.g., a Si atom) is more electropositive than is the latter. The effects of the Y group in the C═Y unit on relative energies are $SiH_2 < CH_2 < PH < NH < S < O$ and $SiH_2 < CH_2 < PH < S < NH < O$ for the 1- and 2-substituted series, respectively.

(3) The effects of the substituent X on the relative energies in the 1-substituted series are $H > NH_2 > CH_3 > F > OH$ ($Y = SiH_2$), $H < CH_3 < F < OH < NH_2$ ($Y = PH$), and $H < CH_3 < OH < F < NH_2$ ($Y = S$), while in the 2-substituted series, the order is $H > CH_3 > F > OH > NH_2$ for all the functional groups.

(4) MPA indicates that the tautomeric interconversions proceed through an $H^{\delta-}$ (hydride) transfer for the series $Y = SiH_2$, PH, and S; in the cases where $Y = CH_2$, NH, and O, an $H^{\delta+}$ (proton) transfer takes place.

(5) We have found that both the Hammond postulate and Pearson's principle of hard and soft acids and bases are operative in these tautomeric processes.

(6) The barriers to enolization, which range from 36 to 61 kcal/mol, are rather high but are considerably lower than those computed for their analogues with second-row atoms. The effect that the Y unit of the functional group C═Y has on increasing the energy barriers occurs in the sequence $SiH_2 < S < PH$, except for the 2-substituted series, in which the order is $SiH_2 < PH < S$ when $X = NH_2$, OH, and F.

(7) The effects of the substituents X on energy barriers depend on the site of substitution, with the trends following the order $H > CH_3 > F > OH > NH_2$ ($Y = SiH_2$) and $F > H > OH > CH_3 > NH_2$ ($Y = PH$ and $Y = S$) in the 1-substituted series, and $H > CH_3 > F > OH > NH_2$ for all the functional groups in the 2-substituted cases.

(8) There is a very good linear correlation between the energy barriers and the Hammett substituent resonance parameters (σ_R), when considering that the correlation coefficient R ranges from 0.9739 to 0.9940 for the case when $Y = SiH_2$ in the 1-substituted series and for all cases in the 2-substituted series.

Acknowledgment. We gratefully acknowledge the continued financial support of the National Science Council of the Republic of China. We are indebted to the National Center for High-Performance Computing for a generous allocation of SRU on the IBM SMP SP2, Fujitsu VPP300, and HP SPP2000. We thank Professor T. H. Yan for many helpful discussions in organic chemistry.

Supporting Information Available: Tables of optimized geometry parameters and bond energies and a profile of the MPA in PDF. This material is available via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Iglesias, E. *J. Org. Chem.* **2003**, *68*, 2680. (b) Bharatam, P. V.; Lammertsma, K. *J. Org. Chem.* **2000**, *65*, 4662. (c) Sobolewski, A. L.; Domcke, W. *Chem. Phys.* **1998**, *232*, 257. (d) *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1990. (e) Capon, B.; Guo, B. Z.; Kowk, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135. (f) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442. (g) Kresge, A. J. *CHEMTECH* **1986**, *16*, 250. (h) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1. (i) Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev.* **1979**, *48*, 107.

(2) (a) Andres, J.; Domingo, L. R.; Picher, M. T.; Safont, V. S. *Int. J. Quantum Chem.* **1998**, *66*, 9. (b) Frau, J.; Donoso, J.; Munoz, F.; Blanco, F. G. *J. Mol. Struct.* **1997**, *390*, 255. (c) Kless, A.; Borner, A.; Heller, D.; Selke, R. *Organometallics* **1997**, *16*, 2096. (d) Jabin, I.; Revial, G.; Tomas, A.; Lemoine, P.; Pfau, M. *Tetrahedron: Asymmetry* **1995**, *6*, 1795. (e) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642.

(3) (a) Long, J. A.; Harris, N. J.; Lammertsma, K. *J. Org. Chem.* **2001**, *66*, 6762. (b) Enchev, V.; Ivanova, G.; Ugrinov, A.; Neykov, G. D.; Minchev, S.; Stoyanov, N. *J. Mol. Struct*. **1998**, *440*, 227. (c) Lee, K. K. H.; Wong, W. T. *J. Organomet. Chem.* **1997**, *547*, 329. (d) Glaser, R.; Murmann, R. K.; Barnes, C. L. *J. Org. Chem*. **1996**, *61*, 1047. (e) Komaromi, I.; Tronchet, J. M. J. *J. Mol. Struct*. **1996**, *366*, 147. (f) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1993**, *115*, 2348.

(4) (a) Albert, J.; Gonzalez, A.; Granell, J.; Moragas, R.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1781. (b) Albert, J.; Gonzalez, A.; Granell, J.; Moragas, R.; Puerta, C.; Valerga, P. *Organometallics* **1997**, *16*, 3775. (c) Mazurek, A. P.; Skulski, L.; Dobrowolski, J. C. *J. Mol. Struct.* **1997**, *410*, 421.

(5) Neto, J. D. D.; Dealencastro, R. B. *Int. J. Quantum Chem.* **1993**, *20*, 107.

(6) Erlenmeyer, E. *Chem. Ber.* **1881**, *14*, 320.

(7) (a) Bergens, S. H.; Bosnich, B. J. *J. Am. Chem. Soc.* **1991**, *113*, 958. (b) Harold, H. *Chem. Rev.* **1979**, *79*, 515. (c) Saito, S. *J. Chem. Phys. Lett.* **1976**, *42*, 399. (d) Blank, B.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 506. (e) Hay, J. M.; Lyon, D. *Nature* **1967**, *216*, 790. (f) Lovering, E. G.; Laidler, K. J. *Can. J. Chem.* **1960**, *38*, 2367. (g) Fuson, R. C.; Byers, D. J.; Rabjohn, N. *J. Am. Chem. Soc.* **1941**, *63*, 2639. (h) Fuson, R. C.; Corse, J.; McKeever C. H. *J. Am. Chem. Soc.* **1940**, *62*, 3250. (i) Kohler, E. P. *J. Am. Chem. Soc.* **1906**, *36*, 177.

(8) Corey, J. Y.; Corey, E. R.; Gaspar, P. P. *Silicon Chemistry*; Wiley: New York, 1988; Chapter 2, p 15.

(9) (a) Thomas, J. C.; Davies, E. C.; Malick, F. K.; Endreszl, C.; Williams, C. R.; Abbas, M.; Petrella, S.; Swisher, K.; Perron, M.; Edwards, R.; Ostenkowski, P.; Urbanczyk, N.; Wiesend, W. N.; Murray, K. S. *Biotechnol. Prog*. **2003**, *19*, 273. (b) Ohshita, J.; Takayama, H.; Tamai, M.; Iida, T.; Kunai, A. *Organometallics* **2003**, *22*, 2338. (c) Besora, M.; Maseras, F.; Lledos, A.; Eisenstein, O. *Inorg. Chem*. **2002**, *41*, 7105. (d) Mosey, N. J.; Baines, K. M.; Woo, T. K. *J. Am. Chem. Soc*. **2002**, *124*, 13306.

(10) Schubert, U. *Silicon Chemistry*; Springer-Verlag: New York, 1999; p 227.

(11) Bradaric, C. J.; Leigh, W. J. *Organometallics* **1998**, *17*, 645.

(12) Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320.

(13) Gordon, M. S.; Truoung, T. N.; Bonderson, E. K. *J. Am. Chem. Soc.* **1986**, *108*, 1421.

(14) Olbrich, G. *Chem. Phys. Lett.* **1986**, *130*, 115.

(15) Walsh, E. N.; Griffith, E. J.; Parry, R. W.; Quin, L. D. *Phosphorous Chemistry*; ACS Symposium Series: New York, 1991; p xi.

(16) Neilson, R. H.; Angelov, C. M. in ref 15, Chapter 6 New Derivative Chemistry of Two-Coordinate Phosphines, p 77.

(17) Damani, L. A. *Sulphur-Containing Drugs and Related Organic Compounds*; Wiley: New York, 1989; p 7.

(18) (a) Ventura, O. N.; Kieninger, M.; Denis, P. A. *J. Phys. Chem. A.* **2003**, *107*, 518. (b) Janak, K. E.; Tanski, J. M.; Churchill, D. G.; Parkin, G. J. *Am. Chem. Soc*. **2002**, *124*, 4182. (c) Schmarr, H. G.; Eisenreich, W.; Engel, K. H. *J. Agric. Food Chem.* **2001**, *49*, 5923. (d) Palomo, C.; Oiarbide, M.; Dias, F.; Ortiz, A.; Linden, A. *J. Am. Chem. Soc.* **2001**, *123*, 5602. (e) Lai, C. H.; Su, M. D.; Chu, S. Y. *J. Phys. Chem. A*. **2001**, *105*, 6932.

(19) Li, G. M.; Niu, S.; Segi, M.; Tanaka, K.; Nakajima, T.; Zingaro, R. A.; Reibenspies, J. H.; Hall, M. B. *J. Org. Chem.* **2000**, *65*, 6601.

(20) Castro, E. A. *Chem. Rev.* **1999**, *99*, 3505.

(21) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

(22) (a) Wu, C. C.; Lien, M. H. *J. Phys. Chem.* **1995**, *100*, 594. (b) Su, C. C.; Lin, C. K.; Wu, C. C.; Lien, M. H. *J. Phys. Chem. A* **1999**, *103*, 3289.

(23) Lin, J. F.; Wu, C. C.; Lien, M. H. *J. Phys. Chem.* **1995**, *99*, 16903.

(24) Chuang, C. H.; Lien, M. H. Ab initio study on the effects of substituents and functional groups in the isomerization of 1- and 2-substituted propenes, acetaldimines, and aldehydes. *Eur. J. Org. Chem.* Accepted.

(25) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Pople, J. A. *J. Chem. Phys*. **1982**, *77*, 3654. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213.

(26) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys*. **1989**, *90*, 2154.

(27) (a) Weinhold, F.; Landis, C. R. *Chem. Educ. Res. Pract.* **2001**, *2*, 91. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 (c) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.* **1988**, *169*, 41. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (e) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (f) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (g) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(28) The optimized geometric parameters calculated at the HF/6-31G**, MP2(full)/6-31G*, and B3LYP/6-31G** levels for all structures examined in this study are presented in the Supporting Information (Table S-1).

(29) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(30) See Table S-2 in the Supporting Information.

(31) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(32) (a) Connors, K. A. *Chemical Kinetics*; VCH Publishers: New York, **1990**; p 221. (b) Agmon, N. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 388. (c) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*,197.

(33) The remaining cases are represented in Figure S-1 of the Supporting Information.

(34) Huang, R.; Espenson, J. H. *J. Org. Chem.* **1999**, *64*, 6935.

(35) Patai, S. Supplement A: The Chemistry of Double-bonded Functional Groups; John Wiley & Sons: New York, 1989; Vol. 2, part 2.

(36) (a) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581. (c) Pearson, R. G. *Chem. Brit.* **1967**, *3*, 103. (d) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967. (e) Pearson, R. G. *Science* **1966**, *151*, 172. (f) Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 1201. (g) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(37) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.