CHEMISTRY LETTERS, pp. 805-808, 1986.

AN ELECTROCHEMICAL STUDY OF BENZOYLSILANES AND BENZOYLGERMANES

Kunio MOCHIDA,* Shuko OKUI, Kyoko ICHIKAWA, Osamu KANAKUBO,
Tohru TSUCHIYA,† and Keiji YAMAMOTO*††
Department of Chemistry, Faculty of Sciences, Gakushuin University,
1-5-1 Mejiro, Tokyo 171
†National Chemistry Laboratory for Industry, 1-1 Higashi, Yatabe,
Ibaraki 305
††Department of Chemical Engineering, Tokyo Institute of Technology,
Meguro, Tokyo 152

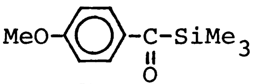
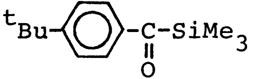
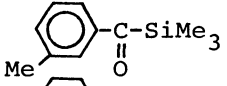
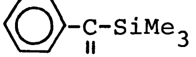
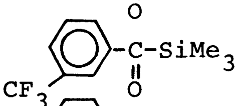
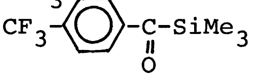
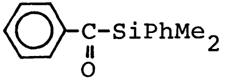
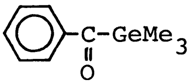
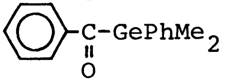
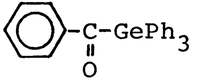
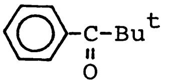
Cyclic voltammetry of seven substituted benzoylsilanes (1) and three benzoylgermanes (2) were investigated. The effects of substituents of 1 and 2 on both cathodic reduction and anodic oxidation potentials were discussed. The cathodic reduction products of 1 were also examined.

Electrochemical studies of ketones and metalloidal ketones have received attention for generating reactive intermediates in organic synthesis.1) While the electrochemistry of ketones has been amply investigated, that of metalloidal ketones has little been studied.2) The present report describes information gained from the first cyclic voltammetry (CV) of seven substituted benzoylsilanes (1) and three benzoylgermanes (2).3)

The redox behaviors of 1 and 2 were examined by CV using acetonitrile-tetraethylammonium perchlorate (TEAP) (0.1 M) as a supporting electrolyte and a glassy carbon working electrode. The reference electrode was Ag/AgCl in acetonitrile. The anodic peak potentials (E_p^{ox}) and cathodic peak potentials (E_p^{red}) of 1 and 2 are listed in Table 1 together with those of pivalophenone (3).4) As typical examples Figures 1-a and b show the single sweep cyclic voltammograms at 100 mV s^{-1} of benzoylphenyldimethylsilane (1g) and benzoylphenyldimethylgermane (2b), respectively. The CV of 1g in Figure 1-a shows that the first wave (W_1), which appears to be an irreversible cathodic peak potential with E_p^{red} = -1.80 V, is followed by an irreversible wave (W_2) with anodic peak potential with E_p^{ox} = 2.02 V. The CV of 2b in Figure 1-b shows the existence of an irreversible reduction (W_1) with E_p^{red} = -1.87 V and an irreversible oxidation (W_2) with E_p^{ox} = 1.73 V.

Information on excited-state interactions is difficult to obtain. Nevertheless, the relative energies of the lowest unoccupied molecular orbitals (LUMO) can be correlated with reduction potentials of redox reactions.5) As shown in Table 1, the cathodic reduction potentials, which are correlated with the lowest π^* level, of 1 and 2 are influenced by both substituents in the phenyl group and at the carbonyl carbon. The reduction potentials of 1d, 2a, and 3 in Table 1 show clearcut evidence that the LUMO's are shifted further downward in 1d and 2a.

Table 1. Cyclic Voltammetry of Substituted Benzoylsilanes, Benzoylgermanes, and Pivalophenone[a)]

Compound	$E_p^{red}/V^{b)}$	$E_p^{ox}/V^{b)}$
 (1a)	-2.04	1.84
 (1b)	-1.94	1.90
 (1c)	-1.89	1.75
 (1d)	-1.98	1.88
 (1e)	-1.63	2.10
 (1f)	-1.60	2.20
 (1g)	-1.80	2.02
 (2a)	-1.93	1.68
 (2b)	-1.87	1.73
 (2c)	-1.72	1.90
 (3)	c)	1.96

a) All potentials were measured in acetonitrile solution containing 0.1 M TEAP at 100 mV s^{-1}. b) Irreversible potential peak. c) Electrolysis of a trace water prevented the observation of potentials.

This trend can be rationalized in terms of larger back-donation effects Si or Ge $\leftarrow C_\pi$ in the excited state than inductive effects $+I_C < +I_{Si\ or\ Ge}$ on the oxygen lone pair n_o.[2,6,7)] The values of E_p^{red} of substituted benzoylsilanes (1a-f) in Table 1 show a distinct dependence on the substituents in the phenyl group. Namely, electron-withdrawing substituents in the phenyl group of 1a-f shift the E_p^{red} upward (the LUMO downward). Figure 2 shows a plot of the E_p^{red} of 1a-f against the Hammett σ constant, and it will be seen that there is a linear relationship (correlation coefficient = 0.923). The difference between the E_p^{red} of 1d and 1g might be attributed to the inductive effect $+I_{SiMe_3} > +I_{SiPhMe_2}$ on the oxygen lone pair. The increasing order of the values of E_p^{red} for benzoylgermanes (2a < 2b < 2c) in Table 1 also depends on the donor properties of the substituents at the

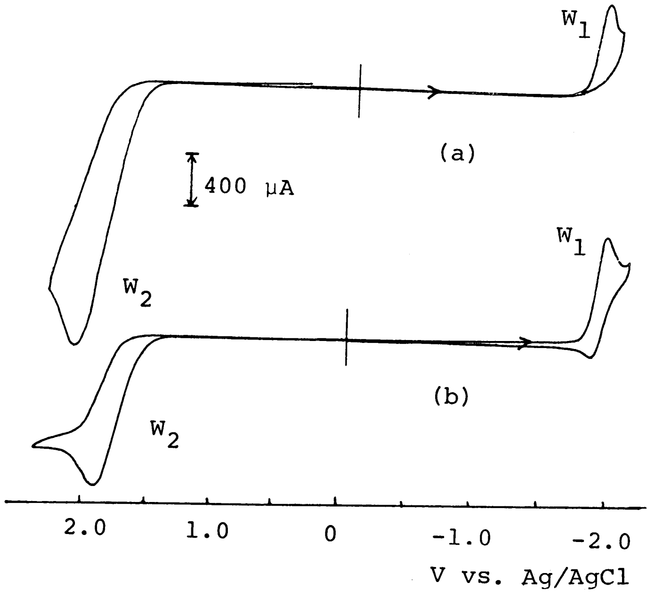


Fig. 1. Single scan cyclic voltammograms of **1g** (upper) and **2b** (lower) at 100 mV s^{-1} in CH_3CN containing 0.1 M TEAP at 25 °C.

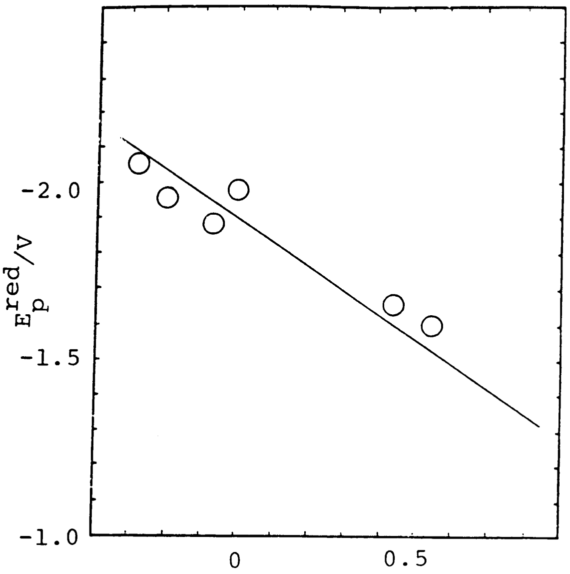
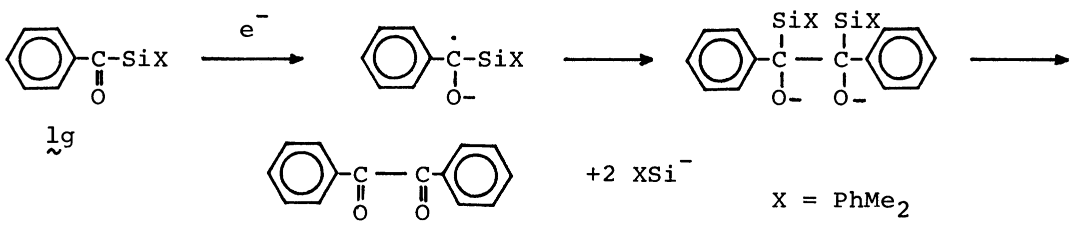


Fig. 2. Plot of the E_p^{red} of **1a-f** versus Hammett σ constant.

carbonyl carbon ($+I_{GeMe_3} > +I_{GePhMe_2} > +I_{GePh_3}$).

The highest occupied molecular orbitals (HOMO) of **1** and **3** have been hitherto discussed as supposedly the n_O level of the oxygen lone pair by the first ionization potentials.[2,8] Recently, correlations of ionization potentials and chemical oxidation potentials of group 4B compounds have been reported.[9,10] The relative energies of the HOMO can be correlated with the E_p^{ox} of **1**, **2**, and **3**. The oxidation potentials of **1d**, **2a**, and **3** in Table 1 show that the HOMO's are shifted upward: **2a** < **1d** < **3**, like the expected order of the inductive effect $+I_C < +I_{Si\ or\ Ge}$. The increasing order of the values of E_p^{ox} of **1a-f** and **2a-c** might be also attributed to the inductive effects of the substituents in the phenyl group for **1a-f** and at the carbonyl carbon for **2a-c**, respectively.

The cathodic reduction of **1** was found to be irreversible, suggesting that the anion radicals of **1** were unstable. Therefore, controlled electrolysis of **1g** at -2.0 V was carried out. After the electrolytic reduction was virtually completed, the reaction mixture was worked up to give benzil (22.0%), phenyldimethylsilanol (9.1%), diphenyltetramethylsiloxane (7.4%) formed from the silanol, and unexpected diphenylmethanol, as main products. The formation of benzil and the silanol may be explained in terms of a mechanism involving dimerization of the initially formed ketyl, followed by elimination of the silyl group as shown in Eq. 1.[11)]



(1)

The ESR studies of the anion radical of **1g** were carried out to confirm the mechanism of electrolysis of **1g**. The ESR spectrum of anion radical of **1g** was stable at -80 °C. When the anion radical of **1g** was allowed to warm at room temperature, a new ESR spectrum of anion radical of benzil appeared. The ESR spectrum of anion radical of benzophenone ketyl was also observed dependent upon the conditions employed when **1g** was reduced with alkali metals.[12,13]

The present electrolysis of **1g** is clearly different from that of the corresponding carbon analogues. The formation of pinacols as main products is well known in electrolysis of aryl ketones.[14]

In this study, we first carried out CV studies of metalloidal ketones. The CV studies of metalloidal ketones will give quite significant information about relative level of HOMO and LUMO of the metalloidal ketones.

We wish to thank Dr. Mitsuo Kira of Tohoku University for valuable discussion.

References

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4) Since each of these oxidative and reductive processes are irreversible, the observed potentials shifted to more positive values relative to $E^{0\ ox}$ and to more negative values relative to $E^{0\ red}$, respectively.

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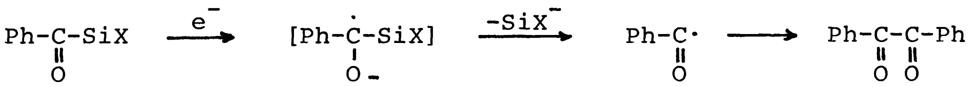
11) The following mechanism is not necessarily excluded.



$$\text{Ph-}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{-SiX} \xrightarrow{e^-} [\text{Ph-}\underset{\overset{|}{\text{O}^-}}{\dot{\text{C}}}\text{-SiX}] \xrightarrow{-\text{SiX}^-} \text{Ph-}\underset{\overset{\|}{\text{O}}}{\text{C}}\cdot \longrightarrow \text{Ph-}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{-}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{-Ph}$$

We thank the referees for constructive criticism on this mechanism.

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(Received January 23, 1986)