p$K_a$. However, additional causes for a pH-dependent $V/K$ isotope effect exist, whose complexities lie beyond the scope of the present discussion.

A clear distinction between protonating mechanisms is established if isotopic discrimination is dependent upon the concentration of substrates. What remains is whether one can identify the nature of the participating group. In the presence of shielding, what portion of the commitment factors suppresses the intramolecular component of isotopic discrimination at high concentrations of substrate will be uncertain. Maximal values of shielded isotopic discrimination may be calculated from eq 18 and 19 after first determining the intrinsic isotope effect through a comparison

of deuterium and tritium isotope effects on $V/K$.[2,7] Because the commitment factors governing the $V/K$ isotope effect are at least as great as those governing intramolecular isotopic discrimination (compare eq 22 to eq 20), minimal values may also be calculated, by substituting the $V/K$ effect for the intrinsic in eq 18 and 19. If isotopic discrimination is less than both minima, the group is monoprotic, if less than the triprotic minimum, it is either a shielded diprotic or a partially shielded monoprotic, if less than the triprotic maximum, all three groups are candidates at various levels of shielding, and if greater than the triprotic maximum, then proton transfer is mediated by an unknown group which cannot be fully shielded from exchange with solvent.

# Communications to the Editor

## First Ionization Band of 1,1-Dimethylsilaethylene by Transient Photoelectron Spectroscopy

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The properties of alkenes and arenes containing trigonal silicon atoms have attracted the recent attention of both experimentalists[1] and theoreticians.[2] This interest derives, in part, from the fact that such compounds are not isolable in the ordinary sense. 1,1-Dimethylsilaethylene (**1**) is such a compound, and we presently wish to report our observation of the first band of its photoelectron spectrum.

The instrument used here was designed[3] to allow chemical studies on the same samples that give rise to the observed spectra and to permit variable distance between generating reaction and photoionization [He I, 584 Å]. Figure 1 summarizes our transient photoelectron (TPE) spectral results on the pyrolysis of 1,1-dimethylsilacyclobutane (**2**, Scheme I).[4]

The lower trace shows the PE spectrum of the precursor **2**. The middle trace shows the spectrum observed at a pyrolysis temperature of 650 °C and a flight distance from furnace tip to photoionization chamber of 30 cm. This spectrum shows the presence of ethylene, indicating the cracking reaction has proceeded. The main product, under these conditions, is a polymeric oil[4] which coats the 40-cm zone between furnace and cold trap (10 cm downstream from photoionization chamber). The upper trace of Figure 1 shows the spectrum obtained with the furnace (720 °C) tip located 5 mm from the center of the photoionization chamber. The new band at 8.3 eV can be assigned to the first ionization state of **1**.[5]

The mass spectrum of the volatile fraction of material collected on the cold (liquid $N_2$) trap, while the middle spectrum was recorded, showed the presence of the symmetrical dimer (**3**, *m/z* 144, 129). When water was injected into the photoionization chamber, immediately downstream from the furnace, the 8.3-eV
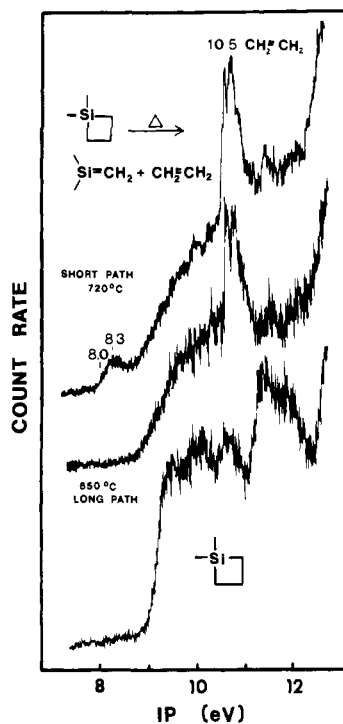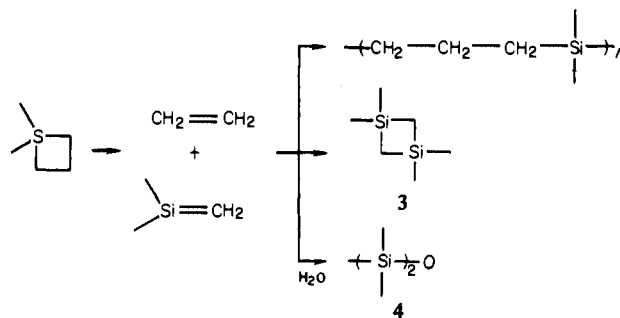


**Figure 1.**

**Scheme I**



photoelectron band disappeared. The mass spectrum of the volatile fraction of material collected on the cold trap when water was present showed new peaks, indicating the formation of ether (**4**) (*m/z* 147; **4** – CH$_3$).[4] The result strongly supports the assignment of the 8.3-eV band as the first ionization of **1**.

The presently observed lowest vertical ionization potential is not in very good agreement with the empirically corrected STO-3G Koopmans theorem[7] value (7.53 eV). It is in better agreement

(1) Mahaffy, P. G.; Gutowsky, R.; Montgomery, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2855 and references therein.

(2) Pietro, W. J.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 7126.

(3) Imre, D.; Koenig, T. *Chem. Phys. Lett.* **1980**, *73*, 62.

(4) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419.

(5) The middle trace of Figure 1 is a good approximation to the background which should be subtracted from the upper trace to leave the spectrum of **1**. The high background relative to **1** in the upper trace is an indication of the high reactivity of **1** at the pressures needed for the TPE technique.

(6) Houk, K. N.; Strozier, P. W.; Santiago, C.; Candor, R. W.; Vollhardt, K. P. *J. Am. Chem. Soc.* **1979**, *101*, 5183.

with the estimate (8.6 eV) yielded by perturbation of isobutylene using the procedure reported in studies of silabenzene[8] and 1-silatoluene.[9]

The adiabatic ionization potential, reported recently by Gusel'nikov and Nanetkin[10] (7.5 ± 0.3 eV), lies below the onset of the band in our observed spectra (8.0 eV). Their value could be correct if the Frank–Condon factors for formation of the adiabatic ionic state are of negligible intensity. Such could be the case if the ionic ground state has a perpendicular geometry. The broad gross shape of the presently observed photoelectron band is not inconsistent with such a geometrical change, but the lack of vibrational resolution prevents any definite predictions of the nature of the geometric change accompanying ionization. We hope the present results may stimulate examination of the ionic states of **1** by reliable theoretical methods.

(7) Koopmans, T. *Physicia (Amsterdam)* **1934**, *1*, 104.

(8) Solouki, B.; Bock, H.; Maier, G.; Mihm, G.; Reisenauer *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51.

(9) Bock, H.; Bowling, R. A.; Solouki, B.; Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1980**, *102*, 429.

(10) Gusel'nikov, L. E.; Nametkin, N. S. *J. Organomet. Chem.* **1979**, *169*, 155.

# A Possible Nucleophilic Ipso-Aromatic Substitution with a Benzyl Anion as the Leaving Group[1]

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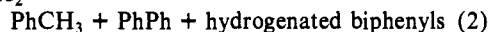
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*Received October 20, 1980*

We report here two examples of ipso-aromatic substitution when diphenylmethane alone, eq 1, or diphenylmethane plus benzene,
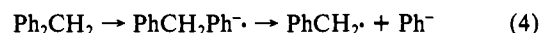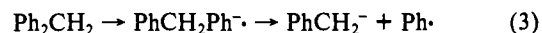
$$Ph_2CH_2 \longrightarrow PhCH_3 + PhCH_2\text{-}C_6H_5 \quad (1)$$
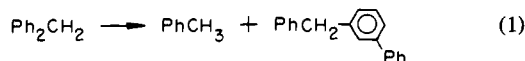
eq 2, are treated with NaK at 0 °C for 3 h in a mixture of glyme

$$C_6H_6 + Ph_2CH_2 \rightarrow$$
$$PhCH_3 + PhPh + \text{hydrogenated biphenyls} \quad (2)$$

and triglyme. That the latter reaction is indeed an ipso reaction between benzene and diphenylmethane and the biphenyl and hydrogenated biphenyls are not produced through dimerization of benzene[2] was shown by labeling the diphenylmethane with carbon-14 (in the phenyl) and demonstrating that the $C_{12}$ products obtained from the labeled reactant contain carbon-14. The biphenyl was also labeled when the reaction was carried out with benzene-$^{14}C$ and diphenylmethane.

We demonstrated earlier[3] that NaK in glyme–triglyme for 3 h at 0 °C cleaves bibenzyl (water quench) to yield toluene. Similarly, 1,2-diphenylpropane yields toluene and ethylbenzene. There are other minor products formed by interaction of the

organic reactants with solvent.[4] Remarkably, diphenylmethane under the same conditions yields toluene[3] (43%) and another product (33%) which we have now definitely identified by independent synthesis as 3-benzylbiphenyl[5] (eq 1). Phenyl-*p*-tolyl-methane undergoes a completely analogous reaction to yield *p*-xylene and 4-methylbenzylbiphenyl. In neither of the latter two reaction products could we find a trace of benzene, even with $^{14}C$-ring-labeled diphenylmethane as the starting material (the carbon-14 provides a sensitive method for the detection of benzene, if it were present). This observation rules out a mechanism involving direct fragmentation of the sp³–sp² bond such as shown in eq 3 or 4 followed by attack of Ph· or Ph⁻ on diphenylmethane

$$Ph_2CH_2 \rightarrow PhCH_2Ph^{-}\cdot \rightarrow PhCH_2^{-} + Ph\cdot \quad (3)$$

$$Ph_2CH_2 \rightarrow PhCH_2Ph^{-}\cdot \rightarrow PhCH_2\cdot + Ph^{-} \quad (4)$$

to produce 3-benzylbiphenyl, since it would be expected that either phenyl radical[6] or phenyl anion should react with solvent to produce benzene. Further, the highly selective formation of 3-benzylbiphenyl provides another argument against attack of Ph· on diphenylmethane, since such attack should produce a mixture of the *o*-, *m*-, and *p*-biphenyls.[7] The mechanism shown in eq 5–8





$$PhCH_2 + H_2O \rightarrow PhCH_3 + \bar{O}H \quad (7)$$
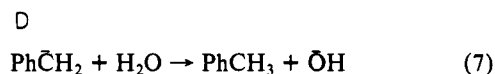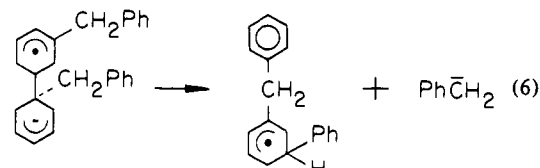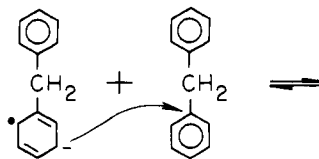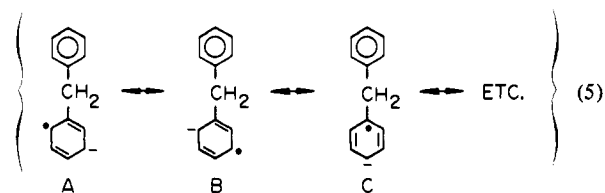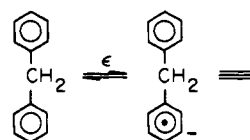
is consistent with all of the facts.[8] Another possibility, suggested by Professor E. Grovenstein, is dimerization of two radical anions, which for convenience can be written in their resonance forms

(1) Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

(2) Grovenstein, E., Jr.; E.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800. When the reaction is carried out with benzene alone (NaK, glyme–triglyme, 0 °C, 3 h), there are only traces of reaction products of benzene detectable. For a discussion of ipso reactions with radicals see: Tiecco, M. *Pure Appl. Chem.* **1981**, *53*, 239.

(3) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851.

(4) In addition to toluene (85%), bibenzyl yielded[3] 11% of a second product which has now been identified (¹H, ¹³C NMR) as 1,2-diphenylbutane.

(5) The method of synthesis was 3-methylbiphenyl —NBS→ 3-PhC₆H₄CH₂Br —DMSO/NaHCO₃→ 3-PhC₆H₄CHO —PhMgBr→ 3-PhC₆H₄CHOHPh —SOCl₂→ —LAH/THF→ 3-PhC₆H₄CH₂Ph. The proton and ¹³C NMR spectra were identical with those of the product from eq 1. 3-Benzylbiphenyl (mp 47 °C) has been previously synthesized by: Chel'tsova, M. A.; Petrov, A. D.; Lubuzh, E. D.; Eremeeva, T. E. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1965**, *14*, 107.

(6) Kryger, R. D.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

(7) For a discussion of partial rate factors for attack of phenyl radicals on aromatic substrates, see: Perkins, M. J. *Free Radicals* **1973**, *2*, 231.

(8) For evidence that radicals are converted to anions in glyme in the presence of alkali metals, see: Garst, J. E. *Acc. Chem. Res.* **1971**, *4*, 400.