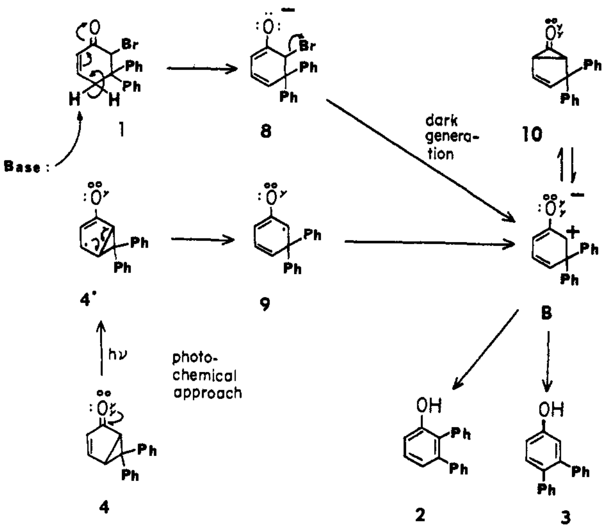
The most striking feature was the identical points obtained from the dark and photochemical runs. Thus, not only were the same two products obtained from the base treatment of bromo ketone **1** as in the photochemical approach, but their distribution and solvent dependency of their distribution proved independent of whether light or base was employed. This provides convincing evidence that there is a precursor common to the two reactions, photochemical and dark.

Actually, bromo ketone **1** had been designed to generate zwitterion B in the absence of light. It was reasoned that enolate **8** obtained in base would be a doubly allylic bromide which would solvolyze with facility to zwitterion B. This mechanism, along with the photochemical approach, is depicted in Chart I.

Chart I. Generation and Rearrangement of Zwitterion B in Dark and Photochemical Approaches



Three additional points are of interest. First, the collapse of zwitterion B to bicyclic enone **4** is forbidden electronically and no **4** is observed from the dark generation of zwitterion B. This establishes that the relatively low efficiency of the photochemical process to give phenols **2** and **3** from bicyclic enone **4** does not derive from reversion of zwitterion B to photochemical reactant. This point could not be established in our earlier photochemical studies. Secondly, although cyclopropanone **10** has been reported as being formed at low temperatures by Chapman[9] from the photolysis of **4**, and despite the possibility of its being formed from the dark reaction presently, it does not account for the cationic rearrangement observed. Nevertheless, it may be present in equilibrium with zwitterion B and such equilibration is electronically allowed. Thirdly, in providing evidence for zwitterion B as an intermediate, the independent generation of B in the dark argues against rearrangement of an electronically excited species as **9** prior to loss of electronic excitation. This agrees with our previously observed migratory aptitude study in which phenyl migrated in preference to cyanophenyl in the type B process.[5] Thus we have defined the stage of the reaction by which electronic relaxation occurs.

It is seen that dark generation of species occurring on surfaces normally accessible photochemically promises to provide an independent means of studying photochemical mechanisms.

Acknowledgment. Support of this research by the National Science Foundation and by National Institutes of Health Grant No. GM-07487, as well as by a predoctoral fellowship to G.A.E., is gratefully acknowledged.

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Received December 27, 1971

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Temperature-Dependent Electron Delocalization in Diphenyldimethylsilane

Sir:

As part of our continuing studies on electron delocalization in silyl compounds,[1] we have investigated compounds of the form $[\mathrm{Ph}(\mathrm{SiR_2})_n\mathrm{Ph}]\cdot^-$, (R = H = Me; n = 1–3) by esr spectroscopy. In $[\mathrm{PhSiMe_2Ph}]\cdot^-$ we have observed what we believe is the first reported example of reversible, temperature-dependent electron delocalization. At low temperatures ($T < -70°$), the unpaired electron in this radical anion is localized on one phenyl ring; at higher temperatures, it appears to be delocalized equally over both phenyl moieties.

Figure 1 shows the esr spectrum of $[\mathrm{PhSiMe_2Ph}]\cdot^-$ at −80°. This radical anion could be generated either chemically (with Na–K alloy in 2:1 2-methyltetrahydrofuran–1,2-dimethoxyethane) or electrolytically (in THF, with tetra-*n*-butylammonium perchlorate as the supporting electrolyte). The hyperfine pattern (2 × 3 × 3) clearly shows the unpaired electron to be localized on one phenyl ring. As first shown by Carrington, *et al.*,[2] the coupling constants may be assigned as follows: $A_{\mathrm{H,p}} = 8.56$ G; $A_{\mathrm{H,o}} = 2.94$ G; $A_{\mathrm{H,m}} = 1.47$ G; $A_{\mathrm{H,SiMe}}$, not observed.

When the temperature of the sample was raised to >−40°, the spectrum shown in Figure 2 appeared. The hyperfine pattern is a triplet of quintets, consistent with electron delocalization over both phenyl rings. The triplet splitting is assigned to hyperfine splitting by the two equivalent para hydrogens ($A_{\mathrm{H,p}} = 4.25$ G), and the quintet to coupling with the four equivalent ortho hydrogens ($A_{\mathrm{H,o}} = 1.37$ G). Neither silyl methyl nor meta hydrogen interaction is apparently observed. This high-temperature spectrum was not due to a decomposition product, since recooling the sample to −80° restored the original spectrum.

Additional support for this interpretation of the temperature effect is given by the relation of the coupling constants of the ortho and para protons for the high- and low-temperature species. The values for both sets of protons in the high-temperature spectrum are approximately one-half those in the low-temperature spectrum, consistent with the decrease by one-half of π-electron density at each site upon delocalization.

Makarov, Kazakova, and Syrkin[3] found the unpaired electron to be localized on one ring at −70°, but reported decomposition of the parent anion radical to $[\mathrm{PhSiMe_2PhSiMe_2Ph}]\cdot^-$ and $[\text{biphenyl}]\cdot^-$ as the temperature was raised to +20°. It is not surprising

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(1) G. R. Husk and R. West, *J. Amer. Chem. Soc.*, 87, 3993 (1965); E. Carberry, R. West, and G. E. Glass, *ibid.*, 91, 5446 (1969).

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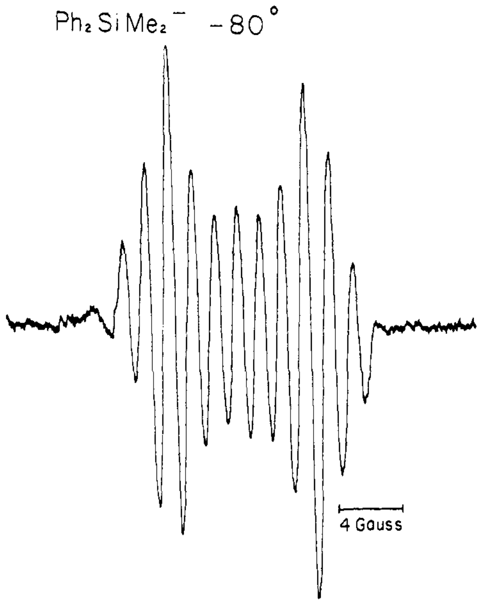

Figure 1. Esr spectrum of $Ph_2SiMe_2\cdot^-$ in THF, −80°.

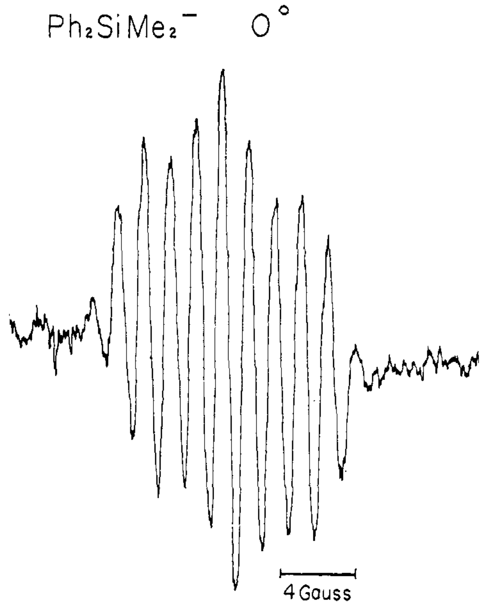

Figure 2. Esr spectrum of $Ph_2SiMe_2\cdot^-$ in THF, 0°.

that the delocalized radical anion was not detected by these workers in view of the limited stability of the parent anion radical. Our studies indicate an approximate half-life for $[PhSiMe_2Ph]\cdot^-$ of 50 min at −95°. Even a moderate delay in obtaining high-temperature spectra would result in decomposition of this species.

If the number of silicon atoms bridging the two phenyl groups was greater than one, delocalization of the electron over two aromatic rings was not observed at any temperature.

The temperature-dependent behavior of diphenyldimethylsilane is in marked contrast to that of the related compound, diphenylmethane.[4] Even at low temperatures ($T < -70°$), the esr spectrum of chemically generated $[PhCH_2Ph]\cdot^-$ consists of 11 equidistant lines which result from splitting by ten approximately equal ring hydrogens ($A_H = 2.23$ G); the two methylene protons cause further splitting. Thus, even at low temperatures, the odd electron is delocalized over both phenyl rings. The next higher homolog, [bibenzyl]$\cdot^-$, is reported to show no delocalization of the unpaired electron at low temperatures.[4,5] Above −70° the bibenzyl radical anion rapidly decays.[6]

In cases where the odd electron is localized on only one ring, the rate of electron transfer between rings, ν_e, is slow compared to the esr hyperfine coupling constants ($\nu_e < 10^6$ sec^{-1}). If the electron is delocalized over both phenyl groups, ν_e is fast compared to the hyperfine coupling constants ($\nu_e > 10^8$ sec^{-1}). McConnell[6] refers to these as "slow passage" or "fast passage" conditions, respectively. If, however, ν_e is of the same order of magnitude as the hyperfine splittings ($10^6 < \nu_e < 10^8$ sec^{-1}), spectra with novel temperature effects are obtained.[7,8] Often the esr spectrum in this intermediate case assumes an S shape, with sharp components superimposed on the broad background. The line widths of the sharp components vary with temperature.

In $[PhSiMe_2Ph]\cdot^-$, where we observe both slow and fast passage extremes, we have been able to see spectra at temperatures between approximately −80 and −40° which indeed have a broad S shape and whose hyperfine structure line widths show anomalous temperature variation. The temperature interval for this intermediate range is extremely sensitive to variations in concentration, solvent, and method of preparation of the anion radical.

McConnell[7] and Harriman and Maki[8] have attempted to describe the factors controlling the rate of inter-ring intramolecular electron transfer in α,ω-diphenylalkanes and related compounds. Unfortunately, the expressions derived for ν_e contain both implicit and explicit temperature-dependent variables in both exponential and preexponential factors. It is therefore impossible to use the theoretical expressions to explain the results for $[PhSiMe_2Ph]\cdot^-$. In particular, it is not at all clear why this anion radical, out of all the compounds studied to date, shows ν_e to be significantly temperature dependent. At present, we can only state that our results are not inconsistent with the theoretical explanations that have been developed.

Studies on additional diphenyl silyl compounds are being undertaken to further elucidate the electron delocalization process.

Acknowledgment. This research was sponsored by the Air Force Office of Scientific Research (NC), USAF Grant No. AF-AFOSR 70-1904. We also wish to thank Dr. John E. Harriman for helpful discussions on the temperature dependence aspects of the problem.

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Received January 20, 1972

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Molecular Conformation and Electronic Structure. The Solid State Spectrum of a Planar Anil

Sir:

Benzylideneaniline (BA), an isoelectronic analog of *trans*-azobenzene (A) and *trans*-stilbene (S), presents