Figure 2A, that the attachment of apolar groups to poly(ethylenimine), which increases the binding affinity of the polymer for small molecules, produces marked increases in esterolytic activity.

Apolar interactions also manifest themselves in a comparison of two substrates with differing lengths of acyl group in the nitrophenyl ester. Lauroylpoly(ethylenimine) hydrolyzes *p*-nitrophenyl laurate ester more rapidly than it does *p*-nitrophenyl acetate ester, as is evident in Figure 2. For *p*-nitrophenyl laurate[17] the comparative increase over that produced by PEI without acyl side chains is even more striking.

It is thus apparent that N-acylpoly(ethylenimines) of different molecular weights and containing a variety of attached side chains should provide polymers with interesting effects in a number of biochemically important reactions.

[17] Althougn 5×10^{-5} *M* aqueous solutions of nitrophenyl laurate appear clear, we are not absolutely certain that the substrate is completely in solution.

[18] This investigation was supported in part by a grant from the National Science Foundation.

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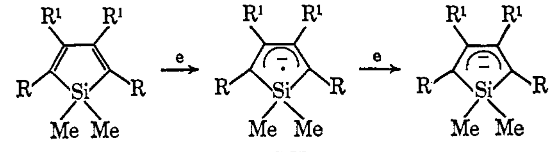
1,4-Disilacyclohexadiene Anion Radicals[1,2]

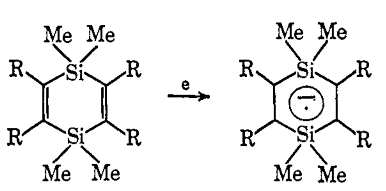
Sir:

In a previous communication the alkali metal reduction of phenyl-substituted silacyclopentadienes to the corresponding radical anions and dianions was described.[1c]



$R = C_6H_5$
$R^1 = H, C_6H_5$

We wish to report on another monocyclic organosilane system, the 1,4-disilacyclohexadiene anion radicals.



Ia, R = H
b, $R = C_6H_5$
c, $R = C_2H_5$
d, R = Me

IIa, R = H
b, $R = C_2H_5$
c, R = Me

These systems are of interest because with silicon providing an unfilled 3d orbital the ions have the same number of π centers and π electrons as well-known carbon analogs with "aromatic" character.

The potassium reduction of Ia in dimethoxyethane (DME) at Dry Ice–acetone temperatures (∼ −70°) gives a five-line esr spectrum which at lower temperatures resolves into the spectrum shown in Figure 1. The reconstructed spectrum assumes 4 equivalent hydrogens with hyperfine splitting (hfs) equal to 3.04 G and 12 equivalent hydrogens with a hfs of 0.24 G. These couplings are assigned to the vinyl and methyl hydrogens of IIa.

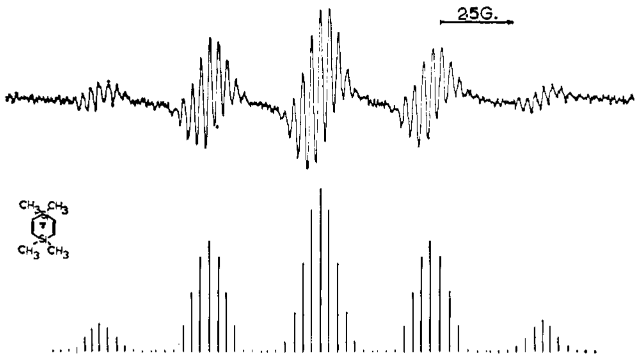


Figure 1.

Support for this structure is obtained from a number of sources. Recently West and coworkers[3] have obtained esr spectra of 1,2-bis(trimethylsilyl)ethylene radical anions by the alkali metal reduction of the corresponding ethylenes. IIa would be expected to be at least as stable. The 0.24-G coupling in IIa is consistent with silyl-methyl hydrogen coupling since this type of coupling varies in the range of 0.14–0.40 G for a variety of organosilane anion radicals.[4,5] A calculated total spin density for the radical is also in agreement with structure IIa. Since a *Q* value of 28 is found to correlate proton coupling with the spin density on the contiguous carbon for a large number of organosilanes,[4,5] the spin density on each carbon atom is 3.04/28 = 0.11.[6] For at least five organosilanes the *Q* value relating the spin density on silicon with the (attached) methyl hydrogen coupling is approximately 1.[4,5] The spin density on each silicon atom is thus ∼0.24, yielding a total calculated spin density of 0.92. This value is in good agreement with structure IIa considering the approximate nature of the *Q* values used.[7]

It is of interest to compare Ia and IIa to benzene and benzene anion radical. The vinyl protons in pmr spectra of Ia appear at exceptionally low fields (τ 3.16). Since the SiMe resonance remains a singlet at −65°, Ia is probably planar.[8] IIa is also probably planar or the conformers are interconverting more rapidly than 10^8 sec^{-1}. The hfs of 3.04 G for IIa compares with 3.75 G for the benzene radical anion.[11] Like benzene radi-

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[1] (a) Organometallic Radicals. III; (b) part I: E. G. Janzen and J. B. Pickett, *J. Am. Chem. Soc.*, **89**, 3649 (1967); (c) part II: E. G. Janzen, J. B. Pickett, and W. H. Atwell, *J. Organometal. Chem.* (Amsterdam), **10**, P6 (1967).

[2] This work is supported by a grant from Dow Corning Corp. Grateful acknowledgment is hereby made.

[3] R. West, Abstracts of the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Paper L64.

[4] M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, 87, 2554 (1965).

[5] Unpublished results in our laboratory.

[6] The McConnell equation, $A^H = Q\rho$, relates the hfs to the spin density: H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

[7] Preliminary Hückel–McLachlan MO calculations using $h = -1.2$ and $k = 0.3$ (see ref 4) give the following spin densities: $\rho_{Si} = 0.194$ and $\rho_C = 0.153$.

[8] Several 1,4-digermacyclohexadienes have been shown to be planar.[9,10] However, steric hindrance between substituents in Ib leads to a loss in coplanarity.[9,10]

[9] M. E. Volpin, V. G. Dulova, Yu. T. Struchkov, N. K. Bokiy, and D. N. Kursanov, *J. Organometal. Chem.* (Amsterdam), **8**, 87 (1967).

[10] N. G. Bokiy and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **6**, 571 (1965).

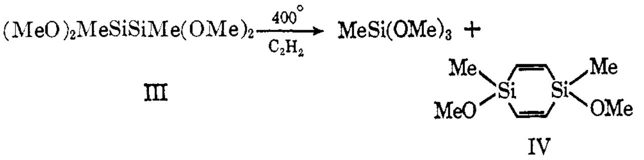
[11] R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964); M. T. Jones, *ibid.*, **88**, 174 (1966). The spectrum of the radical

cal anion, IIa is not stable at room temperature. Disproportionation may be occurring to give the dianion of Ia. We are presently searching for evidence for the formation of this dianion.

Octamethyl-1,4-disilacyclohexadiene gives a small concentration of IId with difficulty. A partially resolved spectrum of 11 multiplets split into 9 lines has been resolved to date. The hfs is 5.32 and 0.18 G which is assigned to the C–Me and Si–Me hydrogens, respectively. The tetraethyl derivative Ic gives a spectrum of nine broad lines which is consistent with coupling to eight methylene protons (hfs 1.93 G). The tetraphenyl derivative Ib is easily reduced, presumably to the dianion. Only an unresolved singlet has been obtained to date with Ib.

All spectra were obtained in DME at Dry Ice–acetone temperatures and are due to the free ions. Further studies on the structure of the ion pairs[1a] are in progress.

Vapor-phase (400°) thermolysis of *sym*-dimethyltetramethoxydisilane (III)[12] in the presence of excess acetylene gave the disilacyclohexadiene IV (60%, bp 100–101° (40 mm)) as a single isomer (SiOMe, SiMe, and –CH at 6.63, 9.85, and 3.08, respectively). *Anal.* Calcd for $C_8H_{16}O_2Si_2$: C, 48.0; H, 8.00; Si, 28.0; mol wt, 200. Found: C, 47.3, 47.8; H, 7.94, 8.17; Si, 28.1, 28.1; mol wt, 200 (mass spectrometry).



$(MeO)_2MeSiSiMe(OMe)_2 \xrightarrow[C_2H_2]{400^\circ} MeSi(OMe)_3 +$

III

IV

Treatment of IV with ethereal MeMgBr gave Ia, bp 158–159° (SiMe and –CH at τ 9.90 and 3.16, respectively). *Anal.* Calcd for $C_8H_{16}Si_2$: C, 57.2; H, 9.52; Si, 33.3; mol wt, 168. Found: C, 57.2, 57.1; H, 9.62, 9.95; Si, 33.3, 33.5; mol wt, 168 (mass spectrometry). Compounds Ic (bp 170–172° (40 mm)) and Id (mp 71–72.5°) were prepared by the general procedure previously described[12] for Ib.

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cation of benzene actually should be compared to IIa, but this radical is unknown. However, the theoretical spin density distribution is identical in the radical anion and cation.

[12] (a) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.* (Amsterdam), **5**, 594 (1966); (b) *Chem. Eng. News*, 30 (Sept 4, 1967).

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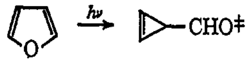
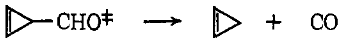
Photoisomerization of 2-Alkylfurans to 3-Alkylfurans

Sir:

In our earlier work on the photochemistry of furan, we had shown that in the vapor phase, on sensitization by mercury ($^3P_1$) atoms[1] or on direct irradiation,[2] an efficient decarbonylation process takes place. In the sensitized reaction, this was postulated to proceed through an initial valence tautomerization to 2-cyclopropenecarboxaldehyde[3] (1a). If eq 1a were reversed, it is possible to regenerate furan in one of two ways which would not be equivalent when a substituent is present. The net reaction, in principle, would lead to a 3-substituted furan from a 2-substituted furan, or *vice versa.* Such over-all transformations (*e.g.*, from 2-aryl to 3-aryl) under the influence of light have been observed in thiophenes,[4] although it is not possible to relate them to the furan system since a ring-contracted product from a reaction analogous to eq 1a or 1b has not been observed in the former instance. Both the analog of eq 1a and its reverse reaction have been reported in the photochemistry of 3,5-diphenylisoxazole,[5] but the resemblance seems to be superficial, as will be pointed out later in this communication.



(1a)



(1b)

We have now observed that 2-methylfuran and 2,5-dimethylfuran photoisomerize to 3-methylfuran and 2,4-dimethylfuran, respectively, under a variety of conditions. Thus, in the vapor phase, direct irradiation or mercury ($^3P_1$) sensitization of 2-methylfuran gave, in addition to CO, 3-methylcyclopropene, and 1,3-butadiene, the identification of which was previously described,[1] an isomeric product (mol wt 82 by mass spectrometry) whose infrared spectrum showed two intense absorptions at 723 and 772 cm^{-1}, in agreement with the reported spectrum[6] of 3-methylfuran. The material was found to be identical with an authentic sample of 3-methylfuran[7] in its retention time on a vapor phase chromatograph and in its infrared spectrum. Irradiation of 2-methylfuran in solution (concentration ~1%) in ether also gave 3-methylfuran.

The quantum yields for the formation of 3-methylfuran and CO + C_4H_6 from 2-methylfuran were dependent on the total pressure in the system, the former increasing slightly with increased pressure and the latter behaving in an inverse manner. The total quantum yield for the photoreaction reached a maximum of 0.80 ± 0.15 at 26 torr when Hg($^3P_1$) was used as a sensitizer. The presence of an eightfold excess of oxygen decreased the quantum yield for the photoisomerization by a factor of four. The fact that the formation of the product was not scavenged completely rules out a free-radical mechanism, *i.e.*, one in which the methyl group migrated from the 2 to the 3 position as a free radical.

Direct irradiation of 2,5-dimethylfuran in the vapor phase gave many isomeric products (mol wt 96 by mass spectrometry) but only one of these was found not to possess a carbonyl group. Its infrared spectrum (gas) showed an intense absorption at 782 cm^{-1} and subsidiary absorptions at 742 and 730 cm^{-1}. The material was identified as 2,4-dimethylfuran by the comparison of its infrared spectrum and its retention time on a

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[1] R. Srinivasan, *J. Am. Chem. Soc.*, **89**, 1758, 4812 (1967).

[2] H. Hiraoka and R. Srinivasan, *J. Chem. Phys.*, in press.

[3] R. Srinivasan, paper presented at the IUPAC Symposium on Organic Photochemistry at Enschede, Holland, July 1967.

[4] H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **89**, 3501 (1967), and earlier references therein.

[5] E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966).

[6] M. Fetizon and J. Guy, *Compt. Rend.*, 1182 (1958).

[7] The authors thank Drs. E. Payo and C. Rivas of the Institute Venezolano de Investigaciones Cientificas, Caracas, Venezuela, for a generous gift of this material.