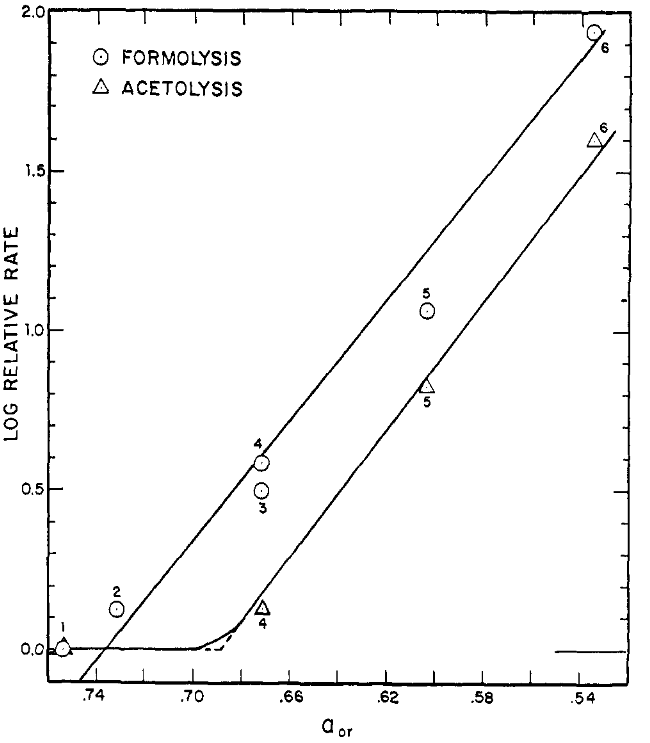

Figure 1.

solvents. The points for formolysis all lie reasonably close to a straight line; the agreement is as good as could be expected, given that the values for a_{or} refer to a system isoconjugate with, but different from, the transition state for assisted solvolysis of I. The plot for acetolysis, on the other hand, consists of two lines intersecting at approximately the point for Ar = α-naphthyl. The general pattern is in complete agreement with our predictions and the results suggest that nucleophilic assistance by the solvent is, as one would expect, less important in formolysis than in acetolysis.

Table I. Rates of Solvolysis of 2-Arylethyl Tosylates (I) at 75°

	Acetic acid		Formic acid	
Tosylate	k, sec^{-1}	k(rel)	k, sec^{-1}	k(rel)
2-Phenylethyl (1)	2.88×10^{-7} [a]	1.00	4.56×10^{-5}	1.00
2-(2-Naphthyl)-ethyl (2)			6.03×10^{-5}	1.32
2-(9-Phenanthryl)-ethyl (3)			1.43×10^{-4}	3.14
2-(1-Naphthyl)-ethyl (4)	3.86×10^{-7}	1.34	1.80×10^{-4}	3.95
2-(1-Pyrenyl)-ethyl (5)	1.99×10^{-6}	6.91	5.27×10^{-4}	11.56
2-(9-Anthryl)-ethyl (6)	1.16×10^{-5} [b]	40.28	4.00×10^{-3} [b]	87.72

[a] Data taken from S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **75**, 147 (1953). [b] Data taken from S. Winstein, *et al.*, *ibid.*, **87**, 3504 (1965).

We are continuing these studies to see how well the scale of nucleophilicities defined in this way agrees with that deduced from the method of Dewar and Sampson.[5] We are also investigating the possibility of applying SCF MO to this problem.

(12) NASA Trainee.

Michael D. Bentley,[12] Michael J. S. Dewar
Department of Chemistry, The University of Texas
Austin, Texas 78712

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Inductive Effects in Acylsilanes and Acyldisilanes

Sir:

The dominant cause of the abnormally long wavelength absorption of acylsilanes and acylgermanes in both the infrared and n–π*[1] ultraviolet regions has been attributed to either inductive effects,[2–5] π(π–d) bonding between the carbonyl group and the metalloid d orbitals,[6,7] or p–d bonding between the lone pair on oxygen and the silicon "d" orbitals.[8] If π(π–d) bonding were the major effect involved, the similarity observed in the spectra of acylsilanes and acylgermanes would not have been expected because of dissimilar degrees of π bonding with 3d(silicon) and 4d(germanium) orbitals,[9] and simple calculations of the type carried out by West[6] show that the energies of the 3d(silicon) orbital and the π* orbital of a simple carbonyl chromophore differ by about 3.4 eV, a magnitude which would not be expected to lead to extensive overlap. However, no direct experimental evidence has existed to clearly establish which of the effects is the dominant one. We suggest the following data serve to remedy this deficiency.

Studies by Gilman,[10] Kumada,[11] and West[12] have shown that an extended orbital, presumably from overlap of d orbitals, encompasses a polysilane system. It has also been shown that π–d overlap exists in vinylsilane systems.[13] As anticipated, when these two systems are brought together a vinylpolysilane system absorbs at longer wavelength in the ultraviolet than does its monosilane analog ($Me_3SiMe_2SiCH{=}CH_2$ λ_{max} 223 mμ (ε 5200);[14] $Me_3SiCH{=}CH_2$ λ_{max} 202 (1470)), because of the overlap of the disilanyl system with the π-type orbitals of the carbon–carbon double bond. It would then be expected, if π(π–d) bonding were an important effect in acylsilanes, that an acyldisilane would similarly absorb at longer wavelength

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(1) It is important to recognize that the wavelengths of the π–π* transitions of analogous acylcarbon, -silicon, and -germanium compounds differ by no more than a few millimicrons, whereas the n–π* transitions differ by 90–100 mμ.

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Table I. Spectral Properties of Acylsilanes and Acyldisilanes

	$Ph_3SiCOCH_3$	$Ph_3SiSiPh_2COCH_3$	$Ph_3SiCOPh$	$Ph_3SiSiPh_2COPh$
Ir,[a] μ	6.08	6.09	6.18	6.19
Uv,[b] λ_{max} (ϵ)				
π–π*	195 (110,000)	219 (40,200)	195 (162,000)	216 (30,500)
		245 (s) (22,900)[c]		244 (48,000)[d]
Phenyl	260 (1450)	268 (s) (9250)	257 (16,200)	
	266 (1410)	275 (s) (5700)		
	272 (1020)			
n–π*	337 (103)	338 (s) (116)	388 (s) (118)	389 (131)
	348 (194)	351 (s) (228)	405 (222)	407 (262)
	362 (360)	363 (380)	424 (293)	423 (342)
	377 (441)	378 (490)	440 (177)	445 (234)
	392 (337)	393 (396)		

[a] In CCl_4 solution. [b] Cyclohexane solvent; s = shoulder. [c] Band at 245 mμ is that due to the phenyldisilanyl system: Ph_6Si_2, λ_{max} 246.5 mμ (ϵ 32,600; see D. N. Hague and R. H. Prince, *J. Chem. Soc.*, 4690 (1965)). [d] Band at 244 mμ is due to overlapping of the 245-mμ band of the $Ph_3SiSiPh_2$ system with the π–π* band at 257 mμ of a benzoylsilane.

than its acylmonosilane analog. In fact, no difference in infrared absorption or long-wavelength ultraviolet absorption is observed, as shown in Tables I and II, and it is evident that in all cases related acyldisilanes and monosilanes have virtually identical absorption spectra. We believe these results clearly demonstrate that π–d bonding is not the dominant effect in acylsilanes and that inductive release from the relatively electropositive silicon (or germanium) atom into the carbonyl system adequately explains the observed long-wavelength infrared carbonyl stretching,[2,3] high basicities,[15] and long-wavelength ultraviolet absorption[2,5] of these compounds.

Table II. Spectral Properties of Acylsilanes and Acyldisilanes

	Ir, μ[a]	Uv,[b] λ_{max} mμ (ϵ)[c]
$Me_3SiCOCH_3$	6.08	323 (18), 333 (34), 346 (62), 358 (100), 372 (126), 388 (93)
$Me_3SiSiMe_2COCH_3$	6.09	370,[d] 384
$CH_3COSiMe_2SiMe_2COCH_3$	6.09	331, 344, 358, 371,[d] 385
$Me_3SiCOPh$	6.18	368 (s) (20), 386 (46), 404 (83), 424 (101), 444 (57)
$Me_3SiSiMe_2COPh$	6.19	405, 424,[d] 442

[a] In CCl_4 solution. [b] Cyclohexane solvent. [c] Where no extinction coefficients are given, the compound is known to be slightly impure. [d] Most intense absorption of the group.

It seems evident, as noted also by a referee, and as Pitt[16] has recognized, that the approach used here is applicable to the study of the interactions of silicon with other neighboring substituents.

While acetyl- and benzoylpentaphenyldisilane could be isolated and purified, the acetyl- and benzoylpentamethyldisilanes and 1,2-bis(acetyl)- and 1,2-bis(benzoyl)-tetramethyldisilanes could not be obtained pure. We believe that the minor contaminants indicated by the nmr and infrared spectra have arisen from cleavage of the disilane bond, presumably by mercuric chloride used in hydrolysis of the 1,3-dithiane system.[17] These species in low concentration would not be expected to affect greatly either the infrared or ultraviolet spectra of the resulting ketones; hence the data given for these compounds are, we believe, significant.

A solution of 2-methyl-2-pentaphenyldisilanyl-1,3-dithiane, mp 275–277° from benzene (*Anal.* Calcd for $C_{35}H_{34}S_2Si_2$: C, 73.13; H, 5.96. Found: C, 73.18; H, 5.90), prepared from pentaphenyldisilanyl chloride[18] and 2-methyl-1,3-dithiane anion according to published procedures,[19] was hydrolyzed over 18 hr at room temperature using excess mercuric chloride–cadmium carbonate in water–benzene–acetone to give 34% of acetylpentaphenyldisilane, mp 165–167° from ethanol-benzene (*Anal.* Calcd for $C_{32}H_{28}OSi_2$: C, 79.29; H, 5.82. Found: C, 79.11; H, 5.86), nmr ($CDCl_3$) three-proton singlet at δ 2.16 ppm, aromatic multiplet (25 protons) at 7–8 ppm.

Benzylpentaphenyldisilane, mp 147–149° from benzene–petroleum ether (bp 80–100°), prepared from benzyldiphenylchlorosilane and triphenylsilyllithium (*Anal.* Calcd for $C_{37}H_{32}Si_2$; C, 83.40; H, 6.05. Found: C, 83.10; H, 5.95), was dibrominated with NBS[2] to give the dibromide in 71% yield (crude), mp 165–167°, which was directly hydrolyzed in benzene–acetone–water with silver trifluoroacetate[2] to give benzoylpentaphenyldisilane, mp 198–200° from benzene–ethanol (*Anal.* Calcd for $C_{37}H_{30}Si_2O$: C, 81.27; H, 5.53. Found: C, 81.19; H, 5.59).

When 2-methyl-2-pentamethyldisilanyl-1,3-dithiane, bp 83–86° (0.1 mm), $n^{22}D$ 1.5384 (*Anal.* Calcd for $C_{10}H_{24}S_2Si_2$: C, 45.38; H, 9.14. Found: C, 45.64; H, 8.88), prepared from 2-methyldithiane anion and pentamethyldisilanyl chloride[20] in 58% yield, was hydrolyzed under the normal conditions, crude acetylpentamethyldisilane was obtained as a colorless oil which could not be completely purified.

Similarly, hydrolysis of 2-phenyl-2-pentamethyldisilanyl-1,3-dithiane, bp 120° (0.02 mm), prepared from 2-phenyl-1,3-dithiane anion and pentamethylchlorodisilane, gave a yellow oil which was partially purified by distillation at reduced pressure but which could not be completely purified by either distillation or glpc due to decomposition.

To 2 equiv of 2-methyl-1,3-dithiane anion was added 1 equiv of 1,2-dichlorotetramethyldisilane[20] to give 50% of 1,2-bis(2-methyl-1,3-dithianyl)tetramethyldisilane, mp 129–130° from benzene–methanol (*Anal.* Calcd for $C_{14}H_{30}S_4Si_2$: C, 43.93; H, 7.90. Found: C, 43.87;

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H, 7.81). Hydrolysis in the usual way gave an oil which decomposed on attempted distillation.

Similarly 1,2-bis(2-phenyl-1,3-dithianyl)tetramethyldisilane was prepared from phenyldithiane anion in 77% yield, mp 274–275° from benzene (*Anal.* Calcd for $C_{24}H_{34}S_4Si_2$: C, 56.86; H, 6.76. Found: C, 57.09; H, 6.73). Attempted hydrolysis gave a yellow oil (C=O stretch 6.19 μ) which could not be completely purified and which decomposed to benzaldehyde on attempted glpc separation.

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(21) Dow Corning Silicones of Canada Fellow, 1966–1967.

A. G. Brook, D. G. Anderson, J. M. Duff
Peter F. Jones,[21] D. M. MacRae
Department of Chemistry, University of Toronto
Toronto 5, Ontario, Canada

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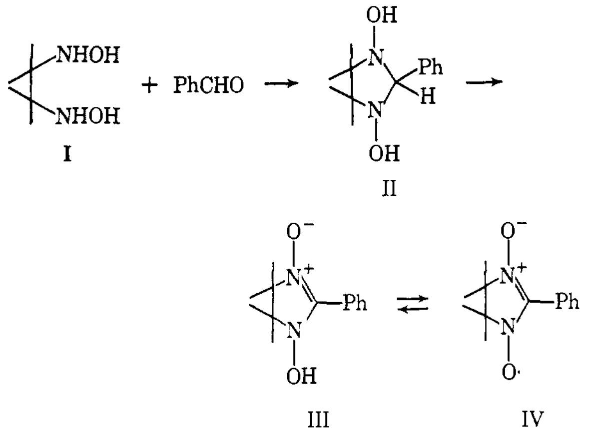
Studies of Free Radicals. I. α-Nitronyl Nitroxides, a New Class of Stable Radicals

Sir:

Although a sizable number of relatively stable free radicals have been described, those classes which are sufficiently stable for isolation and characterization in the presence of oxygen remain quite limited.[1] Notable among these are the nitroxides,[1,2] verdazyls,[3] and phenylhydrazyls[1] together with several individual radicals that owe their stability to exceptional structural relationships (*e.g.*, *peri*-naphthenyl,[4] Koelsch's radical,[5] and galvinoxyl[6]). We now wish to report on the first members of a large new class of radicals of exceptional stability that may find use in spin-labeling techniques[7] and possibly as primary esr standards.

On treatment of the previously known, 2,3-bis(hydroxylamino)-2,3-dimethylbutane[8] (I) with benzaldehyde in benzene solution at room temperature, a product was obtained in 74% yield that was identified as 1,3-dihydroxy-4,4,5,5-tetramethyl-2-phenyltetrahydroimidazole (II) by its analytical and spectral data [ν^{KBr} 3330 cm^{-1} (OH); τ 2.29 (2-NOH), 2.7 (5-ArH), 5.49 (singlet, CH), and 8.93 and 8.97 (2 singlets, 4-CH$_3$) (DMSO); m/e 236 (molecular ion)]. Treatment of a benzene solution of II with excess lead dioxide at room temperature produced an intense blue color. The product IV, isolated quantitatively as blue-black crystals by evaporation of the solvent and recrystallization from ether, displayed an esr spectrum in benzene of five lines in the ratio 1:2:3:2:1, $g = 2.00651 \pm 0.00003$, indicative of two equivalent nitrogen nuclei, $a_N = 7.5$ gauss (benzene). At higher resolution each of the five lines was further split by 0.22 gauss into at least 16 lines due to long-range coupling with the methyl and aromatic hydrogens. As anticipated, solutions of IV showed no nmr signal. Its mass spectrum displayed intense molecular ion, benzoyl, and tetramethylethylene peaks, together with minor fragments at m/e 145 and 162; it had characteristic maxima in the infrared (CHCl$_3$) at 1371,[9] 1140, and 873 (w) cm^{-1} and electronic absorption (EtOH) at 238 mμ (ϵ 9400), 263 (12,200), 360 (13,300), and 588 (685).



(1)

If oxidation of II with lead dioxide was not carried to completion, a highly reactive intermediate could be isolated. This compound was identified as III by its analytical and spectral data [ν^{KBr} 2610 cm^{-1} (hydrogen-bonded OH); $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ (ϵ 11,500) and 317 (ϵ 6000); m/e 234 (molecular ion) and peaks identical with those of IV] and by its formation from IV either by reduction of a dimethoxyethane solution of IV with sodium dispersion or by catalytic hydrogenation. This reduced form III of the radical IV was exceptionally susceptible to oxidizing agents. Thus air, di-*t*-butyl nitroxide, Fremy's salt, and manganese dioxide all yielded IV. The hydrogen affinity of IV must therefore be less than that of the simple nitroxides.

Although solid samples of IV stored in air partially deteriorated during storage for several weeks near a window, samples stored in the darkness appeared to be indefinitely stable. The radical was not decomposed at its melting point (85°) and was unaffected by hot aqueous alkali. Treatment of the radical in benzene with trifluoroacetic acid led to a color change from blue to orange. The resulting solution displayed a 12-line esr spectrum consistent with the asymmetric protonated radical V (R = H), a_N = 5.7 gauss, $a_{N'}$ = 4.5 gauss, and a_H = 4.7 gauss. In agreement with this interpretation, addition of triethylamine to this solution regenerated the blue color and the original five-line esr pattern. By contrast, when trifluoroacetic anhydride was added to a benzene solution of IV a diamagnetic orange solution was obtained. Similarly, an orange solution of IV, which was obtained in 1 *N* aqueous hydrochloric acid, displayed

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