Electron Spin Resonance Studies of Silylketyls[1,2]

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Abstract: The anion radicals (ketyls) of acetyltrimethylsilane, isobutyryltrimethylsilane, pinacolone, and pentamethylacetone have been studied by electron spin resonance spectroscopy. The organosilyl ketyls show larger proton hyperfine splitting constants, higher *g* values, and much broader hyperfine lines than their carbon analogs. These results provide evidence both for the positive inductive effect of silicon and for dative π interaction between the antibonding π^* orbital of the carbonyl group and the silicon atom. A secondary esr spectrum developing when the solutions of silylketyls are warmed is assigned to dimeric anion radicals.

Current interest in the electronic spectra of acylsilanes and -germanes centers around the large bathochromic shift for the $n-\pi^*$ band and the smaller red shift for the $\pi-\pi^*$ band which are observed when an α-carbon atom in a ketone is replaced with a silicon or germanium atom. Several qualitative theories have been offered to account for these shifts to lower energies.

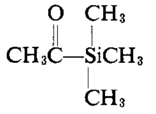
Originally, Brook and his coworkers attributed the shift to dative interactions between the oxygen lone pair and vacant orbitals on the silicon atom.[3,4] Later we,[5] and independently Orgel,[6] suggested that the spectral shifts could be accounted for by dative interactions between the carbonyl π^* orbital and vacant metal orbitals ("excited-state π bonding") accompanied by inductive electron release by the metal. A qualitative correlation diagram showing π^*–d, π–d, and inductive interactions was presented in our paper.[5] Most recently, this model has been questioned by others who have taken the view that inductive effects are primarily or exclusively responsible for the bathochromic shifts in the electronic spectra of silyl and germyl ketones.[7,8]

Extensive molecular orbital calculations supporting the latter view were presented by Agolini, *et al.*, in a recent paper on the electronic spectra of α-metal-substituted carbonyl compounds; they concluded that "the σ-donor property of silicon is primarily responsible for the observed spectral shifts . . . any possible p_π–d_π interactions are of minor importance."[8]

In order to obtain evidence concerning the $\pi^* \rightarrow$ metal π interaction, we have studied electron spin resonance spectra of anion radicals of two α-organosilyl ketones and of the isostructural carbon compounds. In a ketone anion radical, the unpaired electron occupies the π^* level which is also occupied in the electronic excited state in the $n-\pi^*$ and $\pi-\pi^*$ transitions. If π delocalization onto silicon takes place in the electronic excited states, it should influence the esr spectrum of the ketyl. In earlier investigations, esr spectra of anion radicals have provided convincing evidence for dative π bonding, $\pi^* \rightarrow$ metal, in organosilylbenzenes and olefins.[9]

Results and Discussion

Acetyltrimethylsilane (**1**) and isobutyryltrimethylsilane (**2**), a new compound, were synthesized using the 1,3-dithiane route developed by Corey[10] and Brook.[11]



$$CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}CH_3$$

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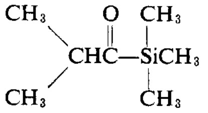

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The ultraviolet spectrum of **2** showed the expected bathochromic shift for the $n-\pi^*$ transition when compared to the corresponding transition for its carbon analog, pentamethylacetone. The ultraviolet spectra for both compounds are reported in the Experimental Section.

Reduction to anion radicals was carried out using potassium metal, either in 2:1 tetrahydrofuran–1,2-dimethoxyethane (THF–DME) or 2:1 2-methyltetrahydrofuran–1,2-dimethoxyethane (MTHF–DME), at -120 to $-40°$. These conditions were chosen so as to minimize ion pairing, which has been observed in related systems.[12,13]

When either **1** or its carbon analog methyl *t*-butyl ketone (pinacolone) is reduced to a radical anion with potassium in mixed ether solvents, the esr spectrum obtained at low temperature consists of a quartet of lines with relative intensities of 1:3:3:1. Figure 1 shows spectra typical of those obtained. The quartet is attributed to the interaction of the unpaired electron with the three equivalent α-protons on the methyl group of the ketyl. Similarly, the potassium radical anions of **2** and its carbon analog isopropyl *t*-butyl ketone (pentamethylacetone) give an esr spectrum consisting of a doublet. Figure 2 illustrates typical spectra obtained under these conditions.

The esr spectra of aliphatic ketyls have been shown to exhibit marked variations with temperature and solvent.[12] In our system, the variations in the hyperfine

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(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract M-146.

(3) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1964).

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(6) L. E. Orgel in "Volatile Organosilicon Compounds," E. A. V. Ebsworth, Ed., Pergamon Press, London, 1963, p 81.

(7) G. J. D. Peddle, *J. Organometal. Chem.* (Amsterdam), **5**, 486 (1966).

(8) F. Agolini, S. Klemenko, J. G. Csismadia, and K. Yates, *Spectrochim. Acta*, **24A**, 16a (1968).

(9) (a) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); (b) A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963); (c) M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965).

(10) E. J. Corey, D. Seebach, and R. Freedman, *ibid.*, **89**, 434 (1967).

(11) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *ibid.*, **89**, 431 (1967).

(12) N. Hirota, *ibid.*, **89**, 32 (1967).

(13) N. Hirota, *J. Chem. Phys.*, **37**, 1881 (1962).

Table I. Comparison of the Electron Spin Resonance Spectra of Anion Radicals

$K^+[RCOM(CH_3)_3]\cdot^-$ R	M	Solvent,[a] temp, °C	$a_{\alpha\text{-H}}$, G	Line width, G	Estimated $a_{\beta\text{-H}}$, G	g^{av}
CH_3	C	A, −90	15.05	0.51	0.06	
		B, −70	15.46	0.63	0.07	2.0037_3
CH_3	Si	A, −90	17.27	1.48	0.16	
		B, −70	17.54	1.56	0.17	2.0040_2
Me_2CH	C	A, −90	2.06	0.58	0.04	
		B, −50	2.31	0.61	0.04	2.0036_4
Me_2CH	Si	A, −90	3.68	1.84	0.17	
		B, −50	4.70	1.92	0.17	2.0039_6

[a] A = 2:1 THF–DME, B = 2:1 MTHF–DME.

splitting constant for the α-proton in the two different solvent systems were small (Table I), but the change with temperature was profound. Table II illustrates the temperature dependence for the radical anion of isobutyryltrimethylsilane in MTHF–DME. The coupling constant and the line width for the α-proton increase with increasing temperature. These results parallel those obtained earlier in studies of the temperature dependence of the ^{13}C splittings of various alkali metal ketyls.[12,13]

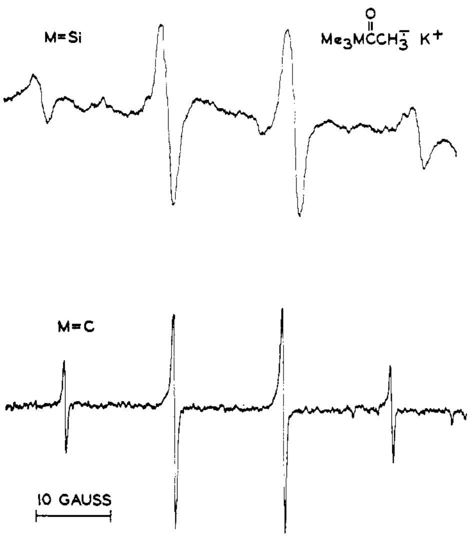


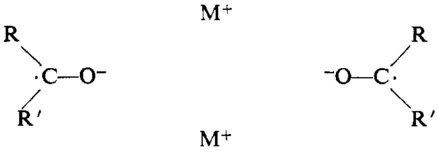
Figure 1. Esr spectra of the potassium radical anions of acetyltrimethylsilylane (upper) and pinacolone (lower).

Table II. Variation of the Hyperfine Coupling Constant for the α-Proton of Potassium Isopropyltrimethylsilylketyl with Temperature[a]

Temp, °C	$a_{\alpha\text{-H}}$, G	Line width, G
−90	3.95	1.82
−70	4.45	1.90
−50	4.70	1.92
−40	4.80	1.95

[a] Determined in 2:1 MTHF–DME.

Hirota has presented evidence that aliphatic ketyls exist in solution as ion quadruplets of type 3 which vary in their degree of solvation with temperature. As temperature increases the ion quadruplets become less highly solvated, and the separation between the positive and negative ions decreases in the ion quadruplet. The increased electrostatic interaction at higher temperature leads to increased charge density and decreased spin density on the ketyl oxygen atom, and therefore to an increase in spin density at the carbonyl carbon atom.[12] A similar argument explains the temperature dependence of the α-proton coupling constants in our system. A salient feature of this argument is that a factor which tends to decrease charge density on the carbonyl carbon atom will produce a larger coupling constant for the α-protons of the ketyl.



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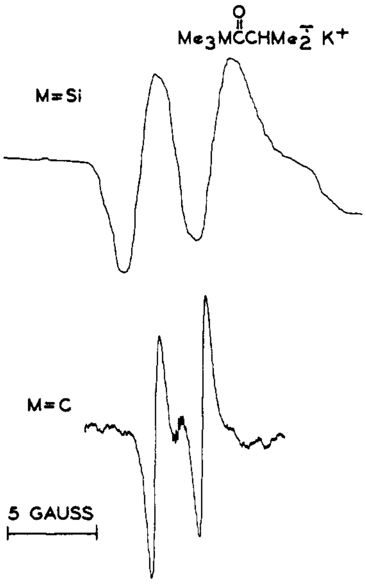

Figure 2. Esr spectra of the potassium radical anions of isobutyryltrimethylsilane (upper) and pentamethylacetone (lower).

Comparison of the data in Table I shows that in both cases the hyperfine splitting constant for the α-protons is somewhat larger for the silicon anion radical than that for the corresponding carbon compound. Following the line of reasoning outlined above, the larger splitting indicates that silicon substitution favors spin rather than charge density on the carbonyl carbon. This is consistent with the well-known +*I* inductive effect of the trimethylsilyl group, and indicates that this effect is significant in considerations of bonding in the acylsilanes. However, the splitting constants for the α-protons of the ketyls give us no information about the extent of π-type interactions in these anion radicals.

Dative π interactions from π^* to the metal should lead to hyperfine coupling by protons on methyl groups attached to silicon. Because of the low temperatures necessary in this study, splittings smaller than about 0.25 G were not resolved. However, in both cases the silylketyls gave much broader lines than the analogous carbon compounds (Figures 1 and 2). The spectra were obtained under identical experimental conditions and there is no intrinsic reason why the silicon-containing anion radicals should give broadened hyperfine lines.[14] Although a small part of the broadening may be due to increased ion pairing with potassium ions, most of the broadening must result from hyperfine interaction with the β-protons.

The β-hyperfine splitting constants were estimated by dividing the observed line width by the expected number of spaces between the hyperfine lines due to the β-protons.[15] The results are given in Table I. The magnitudes are in quite good agreement with similar coupling constants observed in related systems.[16] For instance, Curtis and Allred find quite similar values for t-butyl and trimethylsilyl protons when these are attached to biphenyl anion radicals.[9c,17] For anion radicals of organosilyl olefins, the β-hyperfine coupling constant ranges from about 0.2 to 0.4 G,[18] somewhat larger than estimated for the silylketyls. Delocalization from the olefin π^* level to the metal orbitals is probably more effective than for the carbonyl π^* level, due to better energy matching in the olefin case. A Q value of about 1 relating the hyperfine coupling constant for methylsilyl protons to the spin density on silicon in organosilyl anion radicals has been suggested.[18] If this value applies to the ketyls, the spin density on silicon would be about equal to the splitting constant, or 0.16.

Evidence for dative π interaction from π^* to metal orbitals is also observed from the g values for the four anion radicals considered. In both cases, the silicon ketyls show g values higher by about 0.0003 than their carbon analogs (Table I). A theory has been developed by Stone which relates the measured g value for a free radical to the energy of the molecular orbital occupied by the unpaired electron.[19] The average g factor, g^{av} can be expressed in the form

$$g^{\mathrm{av}} = g_{\mathrm{e}} + b + \lambda c \qquad (1)$$

where g_{e} is the g factor for the free electron, b and c are empirical parameters for the particular system under consideration, and λ represents the coefficient for the resonance integral in the Hückel approximation for the energy of the molecular orbital occupied by the odd electron, $\alpha + \lambda\beta$.[19] In this derivation, β was taken as a negative number, and its coefficient is therefore positive for a bonding orbital and negative for an antibonding orbital. Because we are observing the odd electron in an antibonding orbital, λ is negative in our system. From eq 1 it can be seen that if g_{Si} is greater than g_{C}, then λ_{Si} must be smaller than λ_{C}. Application of this fact to the Hückel expression for the energy of the π^* orbital leads us to the conclusion that the energy of this orbital in a silyl ketyl is lower than the energy of the π^* orbital in the corresponding carbon compound. This is a clear indication that the interaction of silicon's d orbitals with the π^* molecular orbital does lead to a lowering of the energy of this orbital in the acylsilanes.

We conclude that significant π^*–metal π interaction, as well as inductive electron release, takes place in α-silylcarbonyl compounds. This conclusion is confirmed by the contemporaneous work of Bock, Alt, and Seidl,[20] which shows that α-silyl aryl ketones have much lower potentials for reduction to anion radicals than their carbon analogs, and much higher charge-transfer energies in their π complexes with tetracyanoethylene. Bock, Alt, and Seidl present a semiquantitative energy level diagram indicating the operation of both inductive π^*–d and even some ground-state π–d interaction in silylcarbonyl compounds.[20] The original qualitative correlation diagram presented[5] in 1965 showing the operation of all three effects, therefore, appears to be substantially correct.

Dimeric Anion Radicals. When the pale yellow solutions of silylketyls giving rise to the spectra of Figures 1 and 2 were allowed to warm above $-40°$, the yellow gave way to a bright red color and a new esr spectrum appeared. Typical spectra are shown in Figures 3 and 4. The secondary spectrum from acetyltrimethylsilane anion radical (Figure 3) seems best interpreted as a basic septet, of which five lines are clearly observed, further split by two equivalent nuclei of spin $^{3}/_{2}$. A computer simulation based on this assignment is shown in the lower half of Figure 3. Table III lists the hyperfine coupling constants observed for the species. The line width was about 0.6 G, and the g value was 2.00459 ± 0.00005.

Table III. Hyperfine Coupling Constants for the Dimer of the Potassium Ketyl of Acetyltrimethylsilane

Solvent[a]	Temp, °C	$a_{\mathrm{CH_3}}$, G	a_{metal}, G
A	−60	4.55	1.42
	−56	4.55	1.35
	−40	4.55	1.32
B	−90	4.47	1.28
	−80	4.47	1.35
	−70	4.46	1.42

[a] A = 2:1 THF–DME, B = 2:1 MTHF–DME.

Similarly, the potassium radical anion of isopropyl trimethylsilyl ketone, when warmed above $-40°$, gave rise to a new paramagnetic species whose esr spectrum (Figure 4) consisted of a triplet, with $a_{\mathrm{H}} = 2.38$ G, a line width of about 1.3 G, and $g = 2.00486 \pm 0.00005$. No

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(14) In fact, organosilicon anion radicals frequently produce very narrow line spectra.[9]

(15) This is equivalent to dividing the observed line width by the number of β protons. For example, acetyltrimethylsilane and pinacolone each have nine β protons, which would produce ten hyperfine lines or nine spaces. In this estimate, the intrinsic line widths of the β-hyperfine components were neglected.

(16) An independent value of 0.1 G has been reported for β-hyperfine coupling in pentamethylacetone anion radical but was determined under different conditions: N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(17) Curtis and Allred[9c] find $a_{\mathrm{CH_3}}$ = 0.16 and 0.14 for trimethylsilylbiphenylide and bis(trimethylsilyl)biphenylide respectively, coincidentally quite close to our estimated values of 0.16 and 0.17 for the silyl ketyls.

(18) E. G. Janzen, J. B. Pickett, and W. H. Atwell, *J. Am. Chem. Soc.*, **90**, 2719 (1968).

(19) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); **7**, 311 (1964).

(20) H. Bock, H. Alt, and H. Seidl, *J. Am. Chem. Soc.*, in press; private communication with R. W.

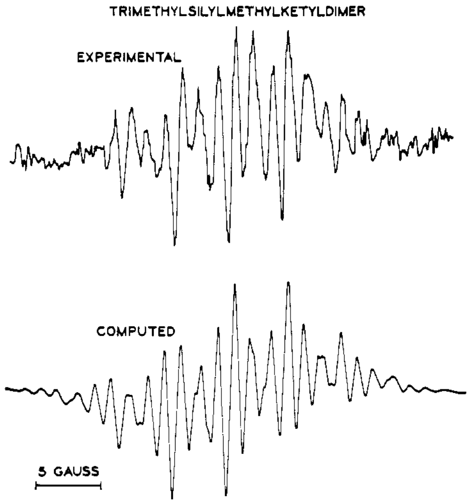
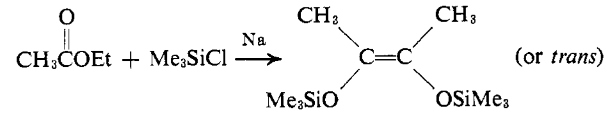


Figure 3. Experimental and simulated esr spectra of the dimer of the radical anion of acetyltrimethylsilane.

metal splitting was observed in this spectrum although the width of the lines may be due to unresolved metal splitting. In both cases the change to the secondary species was irreversible. When the bright red solutions containing the new species were cooled, only broadening of the lines was observed.

The seven-line secondary spectrum obtained with methyltrimethylsilylketyl, and the three-line spectrum obtained with isopropyltrimethylsilylketyl suggest that the new species is a dimer of the original radical anion. A possible (rearranged) dimer of methyl trimethylsilyl ketone radical anion is 2,3-bis(trimethylsiloxy)-2-butene radical anion. In order to determine if this was the species which we were observing in the esr experiment, the 2-butene was synthesized by the method of Ruhlmann and Poredda.[21] The esr spectrum of the



$$CH_3\overset{O}{\overset{\|}{C}}OEt + Me_3SiCl \xrightarrow{Na} (CH_3)(Me_3SiO)C{=}C(CH_3)(OSiMe_3) \quad \text{(or } trans\text{)}$$

potassium radical anion of the compound, obtained under conditions identical with those used for the dimer of methyl trimethylsilyl ketone radical anion, consisted of a simple seven-line pattern with a coupling constant of 7.43 G and a line width of 1.2 G, clearly indicating that the dimer spectra observed in our system could not be attributed to this type of siloxy olefin radical anion.

The temperature variation of the smaller coupling constant observed for the acetyltrimethylsilane ketyl dimer is consistent with the assignment of this coupling constant to the metal (Table IV). The coupling constant of about 1.3 G, however, is much higher than usually observed for potassium ketyls, even in solvents favoring ion pairing.[22] Coupling constants in this range have been observed for potassium when it is chelated between two oxygen atoms in a radical anion. For example, in the radical anion of *o*-dimesitoylbenzene prepared by reduction with potassium, the coupling constant for the metal is 1.33 G.[23] The large coupling constants observed for the metal and the lack of reversibility tend to rule out the equilibria between paramagnetic monomeric and dimeric ketyls which have been demonstrated by Hirota[12] and Luckhurst[24] as a valid explanation for the secondary spectra we have observed. A dimeric structure consistent with our results is shown as **4**. It is an ion quadruplet containing two potassium ions and two 2,3-bis(trimethylsilyl)-2,3-butanediol anion radicals. The latter could be formed by condensation of the anion radical of **1** with a neutral molecule of the ketone.

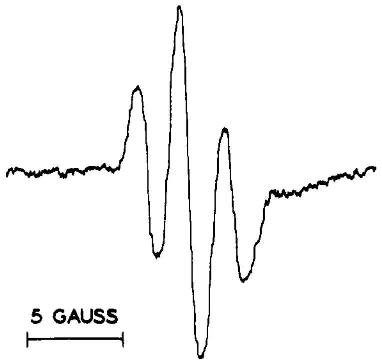
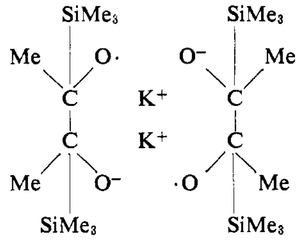


Figure 4. Esr spectrum of the dimer of the radical anion of isopropyl trimethylsilyl ketone.



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Experimental Section

1,3-Dithiane. A solution of 20.0 g (0.185 mol) of 1,3-propanedithiol and 14.1 g (0.185 mol) of methylal in 100 ml of chloroform was added dropwise over a period of 3 hr to a stirred refluxing solution of 10 ml of boron trifluoride etherate in 150 ml of chloroform. After refluxing for an additional hour, the mixture was hydrolyzed with 40 ml of water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness, leaving 21.4 g (96.5%) of a yellow solid, melting at 48–53°. The solid was sublimed at 30° (0.5 mm) to give 17.9 g (80.6%) of pure 1,3-dithiane, mp 52–53° (lit.[25] mp 53°).

2-Methyl-2-trimethylsilyl-1,3-dithiane. Using the procedure outlined by Corey,[10] this compound was prepared in 72% yield from 33.3 mmol of 1,3-dithiane; bp 78–80° (2 torr), $n^{23}\text{D}$ 1.5334 (lit.[10] $n^{20}\text{D}$ 1.5331).

2-Isopropyl-2-trimethylsilyl-1,3-dithiane. To a stirred solution of 49.5 mmol of 2-lithio-1,3-dithiane[26] in 150 ml of tetrahydrofuran at −23° was added 6.45 ml (49.5 mmol) of trimethylchlorosilane. After stirring at −23° for 0.5 hr and at room temperature for 1 hr, the mixture was cooled to −23°, and 32 ml (52.1 mmol) of *n*-butyllithium in hexane was added. The mixture was stirred at −23° for 0.5 hr and at room temperature for 1.0 hr. The green-yellow solution was cooled to −23°, and 5.4 ml (54 mmol) of isopropyl iodide was added. The yellow-green color disappeared gradually while the solution was stirred at room temperature for 5 hr. After hydrolysis with 50 ml of water, the organic layer was separated, and the aqueous layer was extracted three times with ether. The combined ether and tetrahydrofuran layers were dried over anhydrous sodium sulfate, filtered, and distilled to give 8.01 g (68.5%) of pure

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(21) K. Ruhlmann and S. Poredda, *J. Prakt. Chem.*, **12**, 18 (1960).

(22) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963); N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2537 (1964).

(23) B. J. Herold, A. F. Neiva-Correia, and J. D. S. Veiga, *ibid.*, **87**, 2661 (1965).

(24) G. R. Luckhurst, *Mol. Phys.*, **9**, 179 (1965).

(25) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964).

(26) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075 (1965).

2-isopropyl-2-trimethylsilyl-1,3-dithiane: bp 121–123° (2.35 torr); nmr spectrum (CCl_4 with CH_2Cl_2 as internal standard) τ 7.05 and 7.51, dithiane ring proton multiplets; 8.02, methine proton septet, J = 7 Hz; 8.79, $CH(CH_3)_2$ doublet, J = 7 Hz; 9.78, $Si(CH_3)_3$ singlet; ratios, 2:4:1:6:9.

Anal. Calcd for $C_{10}H_{22}S_2Si$: C, 51.22; H, 9.46; S, 27.35. Found: C, 51.15; H, 9.54; S, 27.50.

Acetyltrimethylsilane (1) was prepared in 64% yield using the procedure outlined by Brook.[11]

Isobutyryltrimethylsilane (2). The hydrolysis of 2-isopropyl-2-trimethylsilyl-1,3-dithiane was effected using the method outlined by Brook[11] with the following modifications. When the evolution of gas from the hydrolysis had ceased the reaction mixture was filtered. The filtrate was extracted with five 25-ml portions of ether. The combined ether extracts were washed with three 50-ml portions of water and dried over anhydrous sodium sulfate. The ether solution was filtered and distilled to give 1.43 g (58.2%) of impure isobutyryltrimethylsilane, bp 120–130°. The pure compound was obtained by preparative gas chromatography using a 25 ft × $^3/_8$ in. aluminum column, packed with 25% SE-30 on 40–60 mesh Chromosorb P, operating at 155° with a carrier gas flow of 200 cc of He/min. Under these conditions its retention time is 5 min; infrared spectrum 2965 (s), 2930 (m), 2900 (m), 2870 (m), 1640 (s) (C=O), 1465 (m), 1409 (w), 1377 (m), 1360 (w), 1325 (w), 1250 (s), 1170 (w), 1110 (w), 1065 (m), 990 (m), 860 (s), 830 (s), 750 (m), 695 (m), 620 (m), 365 (m), and 280 cm^{-1} (s); $n^{24}D$ 1.4198; nmr spectrum (CCl_4 with CH_2Cl_2 as an internal standard) τ 7.56, methine septet, J = 6 Hz; 8.05, $-CH(CH_3)_2$ doublet, J = 6 Hz; 9.05, $-Si(CH_3)_3$ singlet; ratios 1:6:9; ultraviolet spectrum (isooctane) λ_{max} 371 mμ (ϵ 119), with shoulders at 343, 357, and 386 mμ and λ_{max} <200 mμ (ϵ >3000).

Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18; Si, 19.46. Found: C, 58.52; H, 11.30; Si, 19.11.

Pinacolone was obtained from the Aldrich Chemical Co., Inc., Milwaukee, Wis., and was used without further purification.

Pentamethylacetone was obtained from Columbia Organic Chemicals Co., Inc., Columbia, S. C. Its purity was verified by gas chromatography prior to use; ultraviolet spectrum (isooctane) λ_{max} 293 (19) and <200 mμ (ϵ>600).

Ketone Radical Anions. The solvents were prepared for use by distillation under a nitrogen atmosphere from lithium aluminum hydride or sodium into a receiver containing anthracene. Sodium–potassium alloy was added to the receivers which were then attached to a vacuum line and degassed until the deep blue color of anthracene radical anion appeared in the solvent. When a sample was being prepared, the appropriate amounts of the solvents to give the indicated *volume* composition were transferred by appropriate high vacuum techniques to a calibrated trap. The solvent mixture was then transferred to a trap containing a mirror of sodium–potassium alloy and used from this reservoir in the preparation of samples.

The samples themselves were prepared in 4-mm quartz sample tubes which were sealed to an 8-mm tube having a side arm and an "O" ring fitting for attaching the sample preparation tube to the vacuum line. The desired reducing metal was placed in the side arm, about 0.01 cc of the desired ketone was placed in the sample tube, and the entire apparatus was attached to the vacuum line. The sample was degassed and sufficient solvent mixture was transferred from the reservoir to fill the sample tube to a height of 40–70 mm. The reducing metal was then distilled from the side arm into the upper portion of the quartz sample tube, and the tube was sealed off. The samples were kept frozen in liquid nitrogen until use. To develop the radical anion, the contents of the sample tube were allowed to warm to slightly above the melting point, the tube was inverted to bring the sample into contact with the mirror, and the sample tube immediately was inserted into the variable-temperature probe of the spectrometer which was cooled to about −120°. As soon as sufficient radical anions had been produced, spectra were recorded at various temperatures up to about −50°. The solutions of all the ketyls were colorless to pale yellow in this temperature range.

Above −40° the solution of the silylketyls became an intense red color as the species giving the secondary spectra slowly developed. This change was not reversible on cooling.

The esr spectra were determined on a Varian Model V4502-13 spectrometer equipped with 100-kc field modulation, dual cavity, and a standard Varian variable-temperature accessory. All of the g values and coupling constants were measured using Fremy's salt (a = 13.00 G, g = 2.00550 ± 0.00005) as a standard in the reference cavity. The values reported in Table I represent averages of at least three separate measurements.

Aromatic Protonation. V. Secondary Hydrogen Isotope Effects on Hydrogen Ion Transfer from the Hydronium Ion[1]

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Abstract: The effect of deuterium substitution in the nonreacting bonds of the hydronium ion on the rate of hydrogen ion transfer from this acid to an aromatic substrate was determined using a method which eliminates primary isotope effects. Measurements were carried out on two substrates, 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene, and, despite the fact that these substances react at rates which differ by 10^3, identical secondary isotope effects were found: $(k_H/k_D)_{sec}$ = 0.59 ± 0.01 at 25°. This result implies that the magnitude of this isotope effect is not sensitive to changes in transition-state structure, at least over the range investigated here. Possible reasons for this behavior are discussed.

Most of the common acids have protons which exchange rapidly with aqueous solvents, and isotope effects on hydrogen ion transfer from these species are therefore usually measured by comparing rates of reaction in light and heavy water In this kind of experiment, the primary isotope effect is necessarily accompanied by a solvent isotope effect, but the latter is likely to be comparatively small.[3] The hydronium ion, however, presents a somewhat special case, for this acid has three readily exchangeable hydrogen atoms. This will introduce a secondary isotope effect into the quantity measured, and this secondary effect, moreover, is likely to be sizeable, for the additional isotopic substitution occurs in "nonreacting" bonds which are very near the reaction site. This expectation is sup-

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(3) R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 251 (1967).