empirical least-squares treatment of Figure 4 to be 97, 97, and 94°, respectively, while the observed values are 94, 92, and 92°. The Pd–bridge Cl bonds opposite the olefinic groups are 0.1 Å longer than the Pd–Cl bond lengths in $(PdCl_2)_n$. However, the ring angles in all three palladium compounds are the same. This observation can be rationalized by invoking the "*trans*" effect and requiring the palladium orbitals to be highly directional in character. This can be contrasted to the $Ni_2Cl_8^{4-}$ anion with a "well-behaved" Ni–Cl–Ni angle of 99.1°. $GaCl_3$ has a Ga–Cl–Ga angle approximately 5° less than that predicted by the Ga–Cl distance of 2.29 Å. Dahl[33] has pointed out that one of the factors leading to anomalously acute bridge angles is metal–metal bonding, and perhaps this is the case in $GaCl_3$.

The empirical nature of the least-squares fit is emphasized by the fact that the slopes are not equal to 1.58 Å, *i.e.*, 0.5 of the average Cl–Cl distance, and the intercepts are not equal to zero. Factors other than Cl–Cl repulsion undoubtedly become relatively more important at the extreme M–Cl distances (2.02 and 2.56 Å), such as inter-ring Cl–Cl repulsions in $[BeCl_2]_n$.

(33) L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 91, 1653 (1969).

Triorganosilicon Acetylacetonates. Enol Ether Isomerism and Stereochemical Lability[1]

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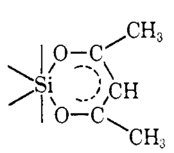
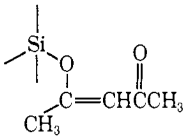
Abstract: Nuclear magnetic resonance studies of triorganosilicon acetylacetonates of the type $R(CH_3)_2Si(acac)$ ($R = n\text{-}C_4H_9$, C_2H_5, CH_3, $CH_2{=}CH$, $CF_3CH_2CH_2$, and C_6H_5), along with $(C_6H_5)_2(CH_3)Si(acac)$, show that the compounds possess an open-chain enol ether structure and give rise to configurations in which the uncoordinated carbonyl oxygen atom is positioned either *cis* or *trans* to the siloxy group. Equilibrium values of the *cis*-to-*trans* ratios in chlorobenzene are dependent on the nature of the substituents on silicon and lie in the range 0.25–0.39. The *cis* isomers undergo a rapid, intramolecular rearrangement process which interchanges the allylic and acetyl methyl groups on the acetylacetonate moiety. First-order rate constants for the stereochemical rearrangements were determined in chlorobenzene solution by nmr line-broadening techniques. In the *cis*-$R(CH_3)_2Si(acac)$ series of compounds, the lability increases in the order $R = n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2{=}CH, C_6H_5 < CF_3CH_2CH_2$. The lability of *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of *cis*-$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. For the rearrangement of *cis*-$(CH_3)_3Si(acac)$, which was studied over the temperature range −36.2–38.4°, the values of the Arrhenius activation energy and frequency factor are 13.8 ± 0.5 kcal/mol and exp(13.05 ± 0.54), respectively. The kinetic data are consistent with a mechanism involving formation of a five-coordinated silicon intermediate. Some proton nmr chemical shift and mass spectral data are presented.

Silicon acetylacetonates[2] may adopt either a chelated (I) or an open-chain enol ether (II) structure, depending on the nature of the other substituents attached to the silicon atom. Neutral compounds of the type $RSi(acac)_2Cl$,[3] $Si(acac)_2(OCOR)_2$,[4,5] and probably $Si(acac)_2Cl_2$[6] have chelated ground-state structures in which silicon achieves a coordination number of six. When less electronegative substituents are present on silicon, as in compounds of the type $R_3Si(acac)$[3,7] or $R_2Si(acac)_2$,[3] four-coordinated silicon enol ether structures are attained.


I


II

In an earlier communication from this laboratory[8] the existence of enol ether isomers for $(CH_3)_3Si(acac)$ was confirmed by nmr spectroscopy. Moreover, the isomer in which the uncoordinated carbonyl group is positioned *cis* to the siloxy group was shown to undergo a rapid intramolecular rearrangement process which interchanges the allylic and acetyl methyl groups on the acetylacetonate moiety. In the present study the kinetics of the rearrangement process has been investigated by nmr line-broadening techniques. Also, a series of new triorganosilicon acetylacetonates has been investigated in order to determine the dependence of the rearrangement rates on the polarity of the silicon substituents.

Experimental Section

Syntheses. All of the triorganosilicon acetylacetonates used in this study were prepared by reaction of stoichiometric amounts of

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(1) Presented in part before the Division of Inorganic Chemistry, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(2) $CH_3COCHCOCH_3^-$, abbreviated acac.

(3) R. West, *J. Amer. Chem. Soc.*, 80, 3246 (1958).

(4) R. M. Pike and R. R. Luongo, *ibid.*, 87, 1403 (1965); 88, 2972 (1966).

(5) C. E. Holloway, R. R. Luongo, and R. M. Pike, *ibid.*, 88, 2060 (1966).

(6) D. W. Thompson, *Inorg. Chem.*, 8, 2015 (1969).

(7) W. H. Knoth, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1954; *cf.* L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, p 14.

(8) J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, 91, 5378 (1969).

Table I. Boiling Points, Yields, and Analytical Results

Compound	Boiling point		% yield	Calcd, %			Found, %		
	°C	mm		C	H	Si	C	H	Si
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	48	0.01	31.5	61.63	10.34	13.1	61.85	10.30	13.5
$(C_2H_5)(CH_3)_2Si(acac)$	80–81	4	31.6	58.01	9.74	15.1	58.29	9.56	14.8
$(CH_2{=}CH)(CH_3)_2Si(acac)$	74–75	4	26.6	58.65	8.75	15.2	58.80	8.81	15.2
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)^a$	54	0.03	46.7	47.23	6.74	11.0	47.27	6.67	12.1
$(C_6H_5)(CH_3)_2Si(acac)$	88–89	0.02	40.5	66.62	7.74	12.0	66.68	7.68	12.1
$(C_6H_5)_2(CH_3)Si(acac)$	140–146	0.05	23.0	72.93	6.80	9.48	72.85	6.78	9.20

[a] This compound was also analyzed for fluorine: calcd, 22.41; found, 22.10.

the approprirate chlorosilane, acetylacetone, and pyridine in hexane solution.[3] The chlorosilanes were obtained from the Chemical Research Department of the Dow Corning Corp., and were fractionally distilled, when necessary, to achieve a purity of 98% or better, as judged by vapor-phase chromatography. Acetylacetone (bp 136–140°) was freshly distilled before use. Hexane was dried by refluxing over calcium hydride. Since the compounds undergo hydrolysis on contact with atmospheric moisture, all reactions and subsequent manipulations of the products were conducted under an atmosphere of dry nitrogen. In general, the triorganochlorosilane (0.250 mol) was added slowly to a stirred solution of acetylacetone (25.6 ml, 0.250 mol) and pyridine (20.1 ml, 0.250 mol) in 100 ml of hexane. Except in the case of the phenylsilyl derivatives, the reaction mixture was heated at reflux temperature and then stirred an additional 20–24 hr at room temperature. The heating times used in the preparation of the $R(CH_3)_2Si(acac)$ compounds were as follows: R = CH_3 and C_2H_5, 5 hr; R = $n\text{-}C_4H_9$, 4.5 hr; R = $CH_2{=}CH$, 3 hr; R = $CF_3CH_2CH_2$, 2.5 hr. $(C_6H_5)(CH_3)_2Si(acac)$ and $(C_6H_5)_2(CH_3)Si(acac)$ were prepared at room temperature by using reaction times of 17 and 12 hr, respectively. Pyridinium chloride was removed from the reaction mixtures by filtration, and hexane was removed under reduced pressure at room temperature. All of the products were purified by vacuum distillation through a 30-cm Vigreux column. The boiling point of $(CH_3)_3Si(acac)$ was in good agreement with the reported value.[3] The boiling points and the percentage yields for the previously unreported compounds are given in Table I along with the analytical results.

Chromatography. Attempts were made to separate the *cis* and *trans* isomers of $(CH_3)_3Si(acac)$ on a dual-column F & M Model 810 gas chromatograph equipped with a thermal conductivity detector cell. The column dimension and packings were as follows: 4 ft × $^1/_4$ in., 10% silmethylene on Chromosorb W; 6 ft × $^1/_4$ in., FS 1265 fluorosilicone gum on an unknown Chromosorb; 6 ft × $^1/_4$ in., SE-30 silicone rubber on Chromosorb W. Numerous chromatograms were obtained under isothermal and temperature-programmed column conditions in the temperature range 100–300°. In all cases there was no separation of the two isomers. Attempts to separate the isomers on 20-ft Carbowax columns at 150–180° with an Aerograph A 90-P3 chromatograph were also unsuccessful.

Mass Spectra. Mass spectra were obtained with an Associated Electrical Industries MS-12 spectrometer equipped with an all-glass inlet system. All spectra were obtained at an ionization potential of 80 eV and a source temperature in the range 160–180°. Perfluorokerosene was used to calibrate the instrument.

Proton Magnetic Resonance Spectra. Proton magnetic resonance spectra were obtained with a Varian A56/60D analytical spectrometer operated at 60.000 MHz. The probe temperature was controlled to ±0.5° with a Varian Model V-6040 temperature controller. Temperatures were determined by measuring the chemical shift differences between the proton resonances of methanol or ethylene glycol and applying the equations of Van Geet.[9] Magnetic field sweep widths were calibrated by the audiofrequency side-band technique. At least three spectral copies were averaged in the determination of line-shape parameters and chemical shift values in order to reduce any error caused by variations in the field sweep. All spectra were recorded at a radiofrequency field strength well below the value necessary to observe the onset of saturation.

Preparation of Solutions. All solutions used in the nmr studies were prepared in a nitrogen-filled glove bag and sealed in nmr tubes which had been previously dried at 150° and cooled in a calcium sulfate desiccator. Carbon tetrachloride, benzene, and chlorobenzene were dried by refluxing over calcium hydride for at least 48 hr. Despite these precautions to avoid hydrolysis, small amounts (2–3%) of free acetylacetone and $(R_3Si)_2O$ could be detected in the nmr spectrum of the solutions after they had aged several days at room temperature. Presumably, these triorganosilicon acetylacetonates undergo slow reaction with hydroxyl groups or strongly bound water on the surface of the glass nmr tubes. The rates of stereochemical rearrangement of the *cis* isomers, however, showed no dependence on the concentration of hydrolysis products.

Results and Discussion

Preparation and Characterization of Compounds. A series of triorganosilicon acetylacetonates of the type $R(CH_3)_2Si(acac)$ (where R = $n\text{-}C_4H_9$, C_2H_5, $CH_2{=}CH$, $CF_3CH_2CH_2$, and C_6H_5), along with $(C_6H_5)_2(CH_3)Si(acac)$ and the previously known compound $(CH_3)_3Si(acac)$,[3,7] has been prepared by reaction of the appropriate triorganochlorosilane and acetylacetone in the presence of pyridine. The compounds are

$$R_3SiCl + H(acac) + py \longrightarrow R_3Si(acac) + [pyH]Cl$$

obtained as high-boiling, colorless to pale yellow liquids. All undergo hydrolysis on contact with atmospheric moisture and slow thermal decomposition at elevated temperatures.

Each compound gave a mass spectral fragmentation pattern consistent with an open-chain enol ether structure. In the $R(CH_3)_2Si(acac)$ series, silicon-containing fragments of the type $R(CH_3)_2Si^+$, $(CH_3)_2Si(acac)^+$, and $R(CH_3)Si(acac)^+$ were generally formed in appreciable amounts. The intensities of these ions are collected in Table II along with the intensity of the most abundant organic species, $C_2H_3O^+$. Also, a weak molecular ion peak was observed for the compounds with R = C_2H_5, CH_3, $CH_2{=}CH$, and $CF_3CH_2CH_2$. The absence of a molecular ion peak for the derivatives with R = $n\text{-}C_4H_9$ and C_6H_5 is attributed to the facile loss of *n*-butyl and methyl groups, respectively, from the parent ions. It is noteworthy that $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$ undergoes extensive rearrangement upon electron impact to give $(CH_3)_2SiF^+$ (m/e 77.0), $(CH_3)SiF_2^+$ (m/e 81.0), SiF_3^+ (m/e 85.0), and $(CH_3)Si(acac)F^+$ (m/e 161) peaks with intensities of 59.8, 7.6, 93.5, and 14.1, respectively. Some degree of rearrangement probably occurs for the other compounds in the $R(CH_3)_2Si(acac)$ series, because weak to moderately intense $(CH_3)SiH_2^+$ (m/e 45.0), $(CH_3)_2SiH^+$ (m/e 59.0), and $(CH_3)_2SiOH^+$ (m/e 75.0) peaks were observed in all cases. The spectrum of $(C_6H_5)_2(CH_3)Si(acac)$ did not contain a molecular ion peak, but $C_2H_3O^+$ was observed as the base ion and $(C_6H_5)(CH_3)Si(acac)^+$ was the most abundant silicon-containing fragment.

The existence of an equilibrium mixture of *cis* (III) and *trans* (IV) enol ether isomers for $(CH_3)_3Si(acac)$ has

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(9) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968); paper presented at the 10th Experimental Nmr Conference, Mellon Institute, Pittsburgh, Pa., Feb 1969.

Table II. Intensities of Selected Ions in the Mass Spectra of Triorganosilicon Acetylacetonates

Compound	Ion			
	$C_2H_3O^{+\,a}$	$R(CH_3)_2Si^{+\,b}$	$(CH_3)_2Si(acac)^{+\,c}$	$R(CH_3)Si(acac)^{+\,b}$
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	55.6	11.1 (115.0)	100.0[d]	27.0 (199.0)
$(C_2H_5)(CH_3)_2Si(acac)$	45.8	38.4 (87.0)	100.0	51.1 (171.0)
$(CH_3)_3Si(acac)$	74.2	96.8 (73.0)	100.0	
$(CH_2{=}CH)(CH_3)_2Si(acac)$	100.0	94.2 (85.0)	32.5	76.7 (169.0)
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	100.0	1.7 (155.0)	65.2	13.0 (239.0)
$(C_6H_5)(CH_3)_2Si(acac)$	49.7	48.5 (135.0)	59.4	100.0 (219.0)

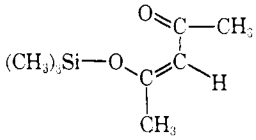
[a] M/e 43.0. [b] M/e values are given in parentheses. [c] M/e 157.0. [d] Ions assigned an intensity of 100.0 represent the most abundant species in each spectrum.

Table III. Proton Chemical Shift Data for *cis*- and *trans*-Triorganosilicon Acetylacetonates[a]

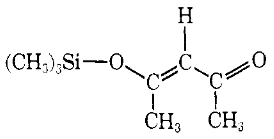
Compound	Solvent	*trans* isomer				*cis* isomer		
		=CH–	$COCH_3$	$=CCH_3$	$SiCH_3$	=CH–	CH_3[b]	$SiCH_3$
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	CCl_4	4.54	7.81	8.00	9.76	4.82	8.03	9.76
$(C_2H_5)(CH_3)_2Si(acac)$	CCl_4	4.53	7.82	8.00	9.76	4.82	8.03	9.76
$(CH_3)_3Si(acac)$	CCl_4	4.53	7.82	8.00	9.74	4.81	8.03	9.74
	C_6H_6[c]	4.45	7.63	8.10	9.95	4.74	8.22	9.95
	d	4.41	7.81	8.00	9.74	4.81	8.01	9.72
$(CH_2{=}CH)(CH_3)_2Si(acac)$	CCl_4	4.50	7.81	8.01	9.69	4.81	8.03	9.67
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	CCl_4	4.51	7.80	7.98	9.69	4.64	8.07	9.73
$(C_6H_5)(CH_3)_2Si(acac)$	CCl_4	4.57	7.82	8.09	9.51	4.83	8.09	9.47
$(C_6H_5)_2(CH_3)Si(acac)$	CCl_4	4.53	7.77	8.14	9.26	4.81	8.11	9.22

[a] All shifts reported as τ values; temperature is 40°; concentration is 10 g/100 ml of solvent unless otherwise noted. [b] Time-averaged acetylacetonate methyl resonance. [c] All shifts in benzene are extrapolated to infinite dilution. [d] Neat liquid.

been previously confirmed by nmr spectroscopy.[8]

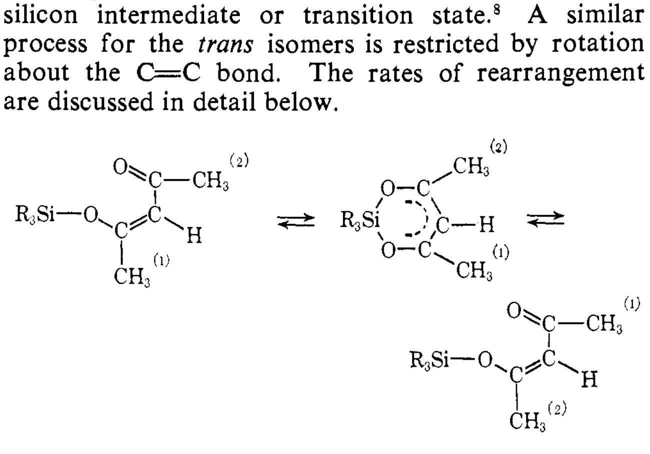


III



IV

Analogous isomers exist for the new silyl derivatives prepared in the present work. The proton nmr spectrum of each *trans* isomer contains a =CH– multiplet, two acetylacetonate methyl doublets, and a Si—CH_3 singlet. Splitting of the acetylacetonate methyl proton lines results from spin–spin coupling between the =CH– proton and both methyl groups. Each of the =CH–, acetylacetonate methyl, and Si—CH_3 regions of the nmr spectra of the *cis* isomers contains one resonance line. The presence of only one acetylacetonate methyl resonance for the *cis* isomers is due to rapid intramolecular rearrangement processes which interchange the nonequivalent acetyl and allylic methyl groups on the acetylacetonate moiety. The rearrangement is believed to occur *via* a five-coordinated silicon intermediate or transition state.[8] A similar process for the *trans* isomers is restricted by rotation about the C=C bond. The rates of rearrangement are discussed in detail below.



Chemical shifts in carbon tetrachloride for the acetylacetonate and Si-CH_3 protons of each compound are collected in Table III; shifts for $(CH_3)_3Si(acac)$ in benzene and as the neat liquid are included for comparison. No significant concentration dependence was observed for $(CH_3)_3Si(acac)$ in carbon tetrachloride over the range 3.0–20.0 g/100 ml of solvent. Since some concentration dependence was found in benzene, the shifts in this solvent were extrapolated to infinite dilution. In each *trans* isomer the magnitude of the coupling between the =CH– and $COCH_3$ protons is ~0.6 Hz, and the allylic coupling constant is 0.4 Hz or less. It is to be noted that the relative chemical shifts for the $COCH_3$ and $=CCH_3$ protons of the *trans* isomer are not in agreement with the empirical "ene-one" rule of Anteunis and Schamp[10] for assigning chemical shifts of similar types of protons in β-diketone enol ethers. However, at least three pieces of evidence can be cited in support of the assignments made here. (1) Replacement of alkyl groups on silicon by phenyl groups leads to 0.09–0.14-ppm upfield shifts for the $=CCH_3$ protons, whereas the $COCH_3$ and =CH– protons show little or no change in chemical shift. An examination of molecular models of the *trans* phenylsilyl derivatives reveals that reasonable configurations are possible in which the $=CCH_3$ protons are within the diamagnetic cone of a phenyl group, but that configurations which can lead to upfield shifts for the $COCH_3$ protons without also appreciably influencing the chemical shifts of the =CH– protons are unlikely. (2) The upfield shifts for the Si-CH_3 protons of both *cis*- and *trans*-$(CH_3)_3Si(acac)$ in benzene solution show that these protons experience the diamagnetic anisotropy of the benzene ring to a greater extent than the internal TMS reference. Apparently, a stereospecific solvent–solute association results from

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(10) M. Anteunis and N. Schamp, *Bull. Soc. Chim. Belg.*, 76, 330 (1967).

the interaction of the π electrons on benzene and the siloxy group.[11] Such an interaction should be expected to lead to upfield shifts for the $=CCH_3$ protons and to downfield shifts for the $COCH_3$ and $=CH-$ protons, which is indeed the result observed for the *trans* isomer. (3) For $(CH_3)_3Si(acac)$ in dichloromethane solution at $-40°$, where the $COCH_3$ and $=CCH_3$ resonances of the *cis* isomer are well resolved (see below), the $=CCH_3$ and $COCH_3$ protons of the *trans* isomer are deshielded by 0.12 ppm and shielded by 0.04 ppm, respectively, relative to the analogous protons of the *cis* isomer. Deshielding of the $=CCH_3$ protons in the *trans* isomer is expected because of the paramagnetic anisotropic effect of the adjacent $COCH_3$ group.[12] Finally, it might be mentioned that for $(CH_3)_3Si(acac)$ at $-40°$, the magnitude of the allylic coupling is slightly greater in the *cis* isomer (~0.5 Hz) than in the *trans* isomer (<0.3 Hz). Under the same conditions, the long-range coupling between the $=CH-$ and $COCH_3$ protons is smaller in the *cis* isomer (~0.0 Hz) than in the *trans* isomer (~0.5 Hz). The relative magnitudes of the allylic coupling are in agreement with the result normally observed for allylic systems, *viz.*, that *cisoid* coupling is slightly larger than *transoid* coupling.[13] The coupling constants alone, however, would not constitute a reliable basis for the chemical shift assignments, because no relationship exists between allylic coupling constants and the stereochemistry of related α,β-unsaturated esters.[14]

Several unsuccessful attempts to separate the *cis* and *trans* isomers of $(CH_3)_3Si(acac)$ by gas chromatography (*cf.* Experimental Section) or by vacuum distillation at 68° through a spinning band column suggest that equilibrium is established readily between the two isomers. Facile isomerization is further supported by the fact that a freshly distilled sample contained the same ratio of isomers as a sample that had aged 6 months at room temperature. Also, after 12 hr at 120° the *cis*-to-*trans* ratio (0.38 ± 0.04) was equal within the 95% confidence level estimated error to the ratio observed at room temperature (0.34 ± 0.04). Both the sample aged at room temperature and the sample heated at 120° should be at equilibrium because the *cis* methyl enol ether of acetylacetone is known to undergo conversion to "pure" *trans* isomer within 8 days at ambient temperature and within 3 hr at 100°.[15] Thus, solutions of the triorganosilicon acetylacetonates in chlorobenzene were assumed to be at equilibrium after 1 week at room temperature, and the *cis*-to-*trans* ratios, shown in Table IV, were determined by planimetric integration of $=CH-$ nmr lines. With the exception of the phenylsilyl derivatives, the equilibrium amount of *cis* isomer increases with increasing electron-withdrawing ability of the substituents on silicon. This relationship between the *cis*-to-*trans* ratios and the polarity of the silicon substituents suggests that a long-range electrostatic interaction may exist between silicon and the dangling carbonyl oxygen atom in the *cis* isomers. Such an interaction would also account, in part, for the enhanced stability of these *cis*-triorganosilicon acetylacetonates relative to the *cis* form of the methyl enol ether of acetylacetone. The *cis*-to-*trans* ratios for $(C_6H_5)(CH_3)_2Si(acac)$ and, especially, $(C_6H_5)_2(CH_3)Si(acac)$ are lower than expected on the basis of inductive effects, but steric factors could weaken the long-range silicon–oxygen interaction in the *cis* isomers of these derivatives.

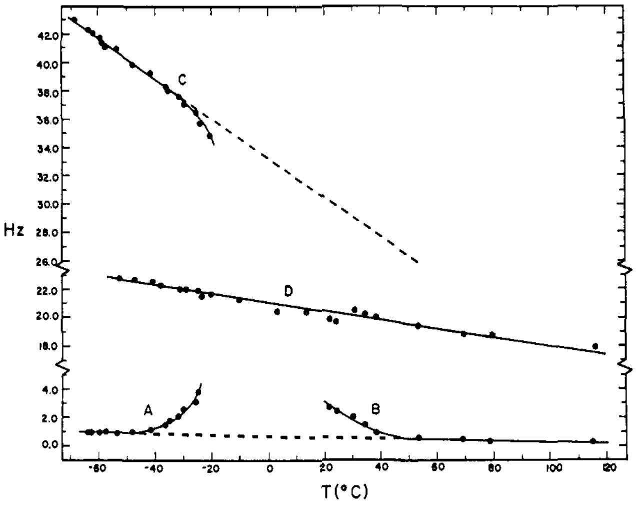

Figure 1. Temperature dependence of nmr line-shape parameters for the acetylacetonate methyl protons of *cis*-$(CH_3)_3Si(acac)$ in chlorobenzene: curve A, line width of the $COCH_3$ resonance; curve B, line width of the time-averaged methyl resonance; curve C, frequency separation between the resonance components, $\delta\nu$. Curve D shows the temperature dependence of $\delta\nu$ for *trans*-$(CH_3)_3Si(acac)$.

Table IV. Equilibrium Ratio of *cis*-to-*trans* Enol Ether Isomers for Triorganosilicon Acetylacetonates[a]

Compound	[*cis*]/[*trans*]
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	0.28[b] ± 0.02[c]
$(C_2H_5)(CH_3)_2Si(acac)$	0.29 ± 0.02
$(CH_3)_3Si(acac)$	0.34 ± 0.04
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	0.39 ± 0.03
$(CH_2{=}CH)(CH_3)_2Si(acac)$	0.38 ± 0.02
$(C_6H_5)(CH_3)_2Si(acac)$	0.31 ± 0.02
$(C_6H_5)_2(CH_3)Si(acac)$	0.25 ± 0.02

[a] In chlorobenzene solution at room temperature; concentration is 0.60 *m*. [b] All values are averages of five spectral copies. [c] Errors are estimated at the 95% confidence level.

Kinetic Studies. In chlorobenzene solution below $-40°$ the interchange of the nonequivalent acetylacetonate methyl groups in *cis*-$(CH_3)_3Si(acac)$ is sufficiently slow to observe two well-resolved methyl proton resonance lines. Above $-40°$ the two lines broaden and merge into a very broad line, which then sharpens above the coalescence temperature.[16] The temperature dependence of the half-widths at half maximum amplitude for the $COCH_3$ resonance below the coalescence temperature and for the time-averaged acetylacetonate methyl resonance above coalescence is shown in Figure 1, curves A and B, respectively.

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(11) Similar stereospecific interactions between benzene and a variety of other types of solute molecules are well known. See, for example, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, pp 841–857.

(12) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).

(13) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(14) R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

(15) B. Eistert, F. Arndt, and L. Loewe, *Chem. Ber.*, **84**, 156 (1951).

(16) An illustration of the temperature dependence of the acetylacetonate methyl resonances of *cis*-$(CH_3)_3Si(acac)$ may be found in ref 8, Figure 2.

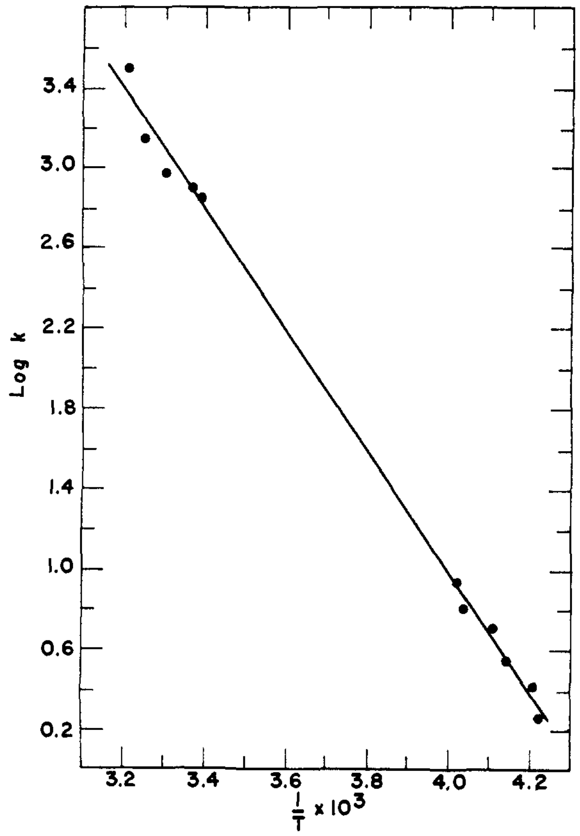

Figure 2. Log k *vs.* $1/T$ plot for *cis*-$(CH_3)_3Si(acac)$ in chlorobenzene solution.

Accurate line widths could not be determined in the region near the coalescence temperature, because the lines were very broad and partially obscured by the acetylacetonate methyl resonances of the *trans* isomer.

Gutowsky and Holm[17] have shown that the mean lifetimes, τ_A and τ_B, of protons exchanging between two nonequivalent sites can be determined from the nmr line shapes if $\delta\nu$, the frequency separation between the resonance components in absence of exchange, and T_2, the transverse relaxation time, are known. The mean lifetimes are related to the quantity τ by $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$. Since the two nonequivalent sites in the systems considered here are equally populated, $\tau_A = \tau_B = 2\tau$. In the region of slow exchange (below $-40°$) $\delta\nu$ for *cis*-$(CH_3)_3Si(acac)$ is temperature dependent, presumably, because of temperature-dependent solvation effects. Since the line widths of both the uncoupled $COCH_3$ resonance in the region of slow exchange and the time-averaged resonance in the region of fast exchange (above 50°) vary with temperature, T_2 is also temperature dependent. The temperature dependence for $\delta\nu$ and T_2 is analogous to the behavior found previously for the nonequivalent methyl protons in chelated metal acetylacetonates.[18,19] Values of $\delta\nu$ in the region of exchange (-36.2–$38.4°$) were obtained by linear extrapolation of data in the region of slow exchange, as shown in Figure 1C. The validity of such an extrapolation is supported by the linear temperature dependence of $\delta\nu$ for the stereochemically rigid *trans* isomer over the same temperature region (Figure 1D). Similarly, values of T_2 in the region of exchange were determined from the extrapolated values of the line widths (*cf.* Figure 1, the dashed line connecting curves A and B). The relaxation times of the $=CCH_3$ protons below coalescence, where they are slightly coupled to the $=CH-$ proton, were assumed to be equal to the relaxation times found for the $COCH_3$ protons.

Values of τ for *cis*-$(CH_3)_3Si(acac)$ in the region of exchange below the coalescence temperature were determined by comparing the observed width at half maximum amplitude of the uncoupled $COCH_3$ resonance with the width calculated from the Gutowsky–Holm equation for various trial values of τ. Although the small coupling between the $-CH=$ and $=CCH_3$ protons below coalescence was not included in the calculated spectra, the error generated in the computed values of τ is estimated to be only $\sim 2\%$. Above the coalescence temperature τ was determined by comparing the observed and computed widths of the time-averaged resonance line. The line widths, extrapolated values of $\delta\nu$, and the computed values of τ in the region of exchange are collected in Table V. A plot of log k *vs.* $1/T$, where $k = (2\tau)^{-1}$, is shown in Figure 2. Within experimental error, the slopes of the best straight lines through the sets of data points above and below the coalescence temperature are equal. Linear least-squares treatment of all 11 data points gave an Arrhenius activation energy and frequency factor of 13.8 ± 0.5 kcal/mol and exp(13.05 ± 0.54), respectively, and an extrapolated value of 851 sec^{-1} for the first-order rate constant at 25°. The errors in the activation parameters are estimated at the 95% confidence level. An activation entropy of -0.8 ± 2.5 eu at 25° was calculated from the frequency factor by assuming that the Eyring equation holds.

Table V. Nmr Line-Shape Parameters and Kinetic Data for *cis*-$(CH_3)_3Si(acac)$[a]

Temp, °C	Line width,[b] Hz	$\delta\nu$, Hz	$10^3\tau$, sec
−36.2	1.57	38.27	276
−35.5	1.82	38.17	194
−31.7	2.17	37.62	137
−29.8	2.68	37.35	96.4
−25.4	3.10	36.72	77.6
−24.4	3.91	36.57	56.7
21.8	2.72	29.84	0.691
24.2	2.45	29.60	0.618
30.3	2.09	28.72	0.525
34.2	1.54	28.16	0.351
38.4	0.98	27.56	0.146

[a] In chlorobenzene solution; concentration is 0.60 *m*. [b] Widths below coalescence (−36.2 to −24.4°) refer to the uncoupled $COCH_3$ resonance component; above coalescence (21.8° to 38.4°) the widths are for the time-averaged acetylacetonate methyl resonance line.

First-order rate constants in chlorobenzene solution for the stereochemical rearrangement of the other *cis*-triorganosilicon acetylacetonates prepared in this study were determined at selected temperatures by using procedures analogous to those described above for *cis*-$(CH_3)_3Si(acac)$. The acetylacetonate methyl proton

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Table VI. Nmr Line-Shape Parameters for the Acetylacetonate Methyl Resonances of *cis*-Triorganosilicon Acetylacetonates[a]

Compound	Temp, °C	Line width,[b] Hz	$\delta\nu$, Hz
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	−23.0	2.51[c] ± 0.05[d]	36.76[e]
$(C_2H_5)(CH_3)_2Si(acac)$	−23.0	2.71 ± 0.05	36.86
$(CH_2{=}CH)(CH_3)_2Si(acac)$	0.7	3.54 ± 0.04	29.92
$(C_6H_5)(CH_3)_2Si(acac)$	−12.7	>10.0	41.40
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	−12.7	1.81 ± 0.02	20.40
$(C_6H_5)_2(CH_3)Si(acac)$	−12.7	3.44 ± 0.04	32.68

[a] In chlorobenzene solution; concentration is 0.60 *m*. [b] Line widths for $(n\text{-}C_4H_9)(CH_3)_2Si(acac)$ and $(C_2H_5)(CH_3)_2Si(acac)$ refer to the $COCH_3$ resonance component below the coalescence temperature; all others are for the time-averaged resonance above caalescence. [c] Average of at least three spectral copies. [d] Errors are for one standard deviation. [e] All values of $\delta\nu$ were obtained by linear extrapolation of the temperature dependence of $\delta\nu$ in the region of slow exchange.

Table VII. Kinetic Data for Acetylacetonate Methyl Group Exchange in *cis*-Triorganosilicon Acetylacetonates[a]

Compound	Temp, °C	k, sec^{-1}	E_a, kcal/mol
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	−23.3	5.35 ± 0.16[b]	14.1
$(C_2H_5)(CH_3)_2Si(acac)$	−23.3	6.96 ± 0.10	14.0
$(CH_2{=}CH)(CH_3)_2Si(acac)$	0.7	500 ± 30	13.0
$(C_6H_5)(CH_3)_2Si(acac)$	−12.7	>91.9, <300	<13.2, >12.6
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	−12.7	621 ± 118	12.2
$(C_6H_5)_2(CH_3)Si(acac)$	−12.7	628 ± 38	12.2

[a] In chlorobenzene solution; total concentration is 0.60 *m*. [b] Basis for estimates of error is described in the text.

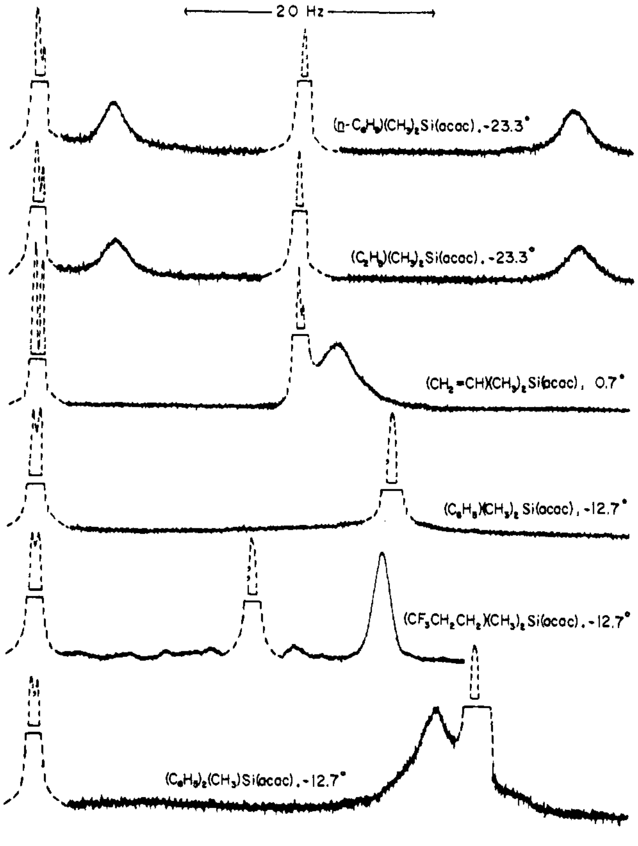

Figure 3. Exchange-broadened acetylacetonate methyl proton resonances for *cis*-triorganosilicon acetylacetonates in chlorobenzene. Dashed lines are the acetylacetonate methyl resonances of the *trans* isomer in each equilibrium mixture. Total concentration is 0.60 *m*.

resonances for each *cis* isomer at each selected temperature are illustrated in Figure 3. Line widths and extrapolated values of $\delta\nu$ are given in Table VI. The uncertainty in the extrapolated value of $\delta\nu$ for *cis*-$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$ is estimated to be *ca.* ±2.0 Hz; for the other *cis* isomers, the uncertainty in $\delta\nu$ is believed to be ±1.0 Hz or less. In the determination of mean lifetimes, the transverse relaxation times were assumed to be equal to those obtained for *cis*-$(CH_3)_3Si(acac)$. This latter assumption is supported by the fact that each *cis* isomer exhibited a time-averaged line width in the limit of fast exchange which was equal to the line width found for *cis*-$(CH_3)_3Si(acac)$ under similar conditions.

It should be noted that for several of the *cis* derivatives, the temperatures at which accurate line widths could be determined were limited by the acetylacetonate methyl resonances of the *trans* isomers present in the equilibrium mixtures (*cf.* Figure 3). In the case of $(C_6H_5)(CH_3)_2Si(acac)$, for example, the time-averaged methyl resonance of the *cis* isomer at −12.7° is so broad that it is barely detectable above the base line. Above −12.7° the time-averaged line is superimposed on $=CCH_3$ resonance of the *trans* isomer, and in the region of exchange below coalescence, the $COCH_3$ resonances of the two isomers are nearly superimposed. Therefore, only an upper or lower limit could be determined for the rate constant at −12.7°. The lower limit was estimated from the simplified Gutowsky-Holm equation,[20] and the upper limit was established by assuming the width of the time-averaged resonance to be >10 Hz.

Values of the first-order constants are shown in Table VII, along with calculated values of the Arrhenius activation energies. The errors in the rate constants for *cis*-$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$ and *cis*-$(C_2H_5)(CH_3)_2Si(acac)$ are based on the uncertainties in the observed line width of the $COCH_3$ resonance; the estimated error in $\delta\nu$ (±1.0 Hz) propagates a very small error (<0.05%) in the rate constant. On the other hand, errors in the rate constants for the other *cis* isomers, which were determined from the widths of the time-averaged lines above coalescence, are due mainly to uncertainties in $\delta\nu$. For example, the error generated in the rate constant for *cis*-$(CH_2{=}CH)(CH_3)_2Si(acac)$ due to the uncertainty in the line width is only 1.0%,

[20] Equation 6 in ref 17.

whereas the error propagated by an uncertainty of ±1.0 Hz in $\delta\nu$ is 6.0%. The activation energies shown in Table VII were calculated from the first-order rate constants by assuming that the frequency factor is equal to the value obtained for *cis*-$(CH_3)_3Si(acac)$.

From the above data it may be concluded that there is a general increase in the rate of acetylacetonate methyl group exchange with increasing polarity of the substituents on silicon. For the *cis*-$R(CH_3)_2Si(acac)$ compounds, the rate increases in the order $R = n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2{=}CH,\ C_6H_5 < CF_3CH_2CH_2$, and the lability of *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. The dependence of the rates on the polarity of the silicon substituents is consistent with a mechanism involving formation of a five-coordinated silicon intermediate or transition state. Although several factors contribute to the energy required for such a bond-making activation process, as the electron-withdrawing ability of the substituents is increased, the resulting increase in positive charge on silicon should facilitate the use of a metal d orbital in achieving the transition state.[21] Relative to the alkyl-substituted silicon derivatives, the phenylsilyl derivatives are less labile than might be expected on the basis of σ inductive effects alone. However, the phenyl group has a greater steric requirement than the other substituents studied and, also, may participate in ligand→metal π bonding. Both of these latter factors would tend to lower the rearrangement rate. Since *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is more labile than *cis*-$(C_6H_5)(CH_3)_2Si(acac)$, however, σ inductive effects must play an important role in determining the *relative* labilities of these derivatives.

Acknowledgment. The support of this research by National Science Foundation Grant No. GP-9503 is gratefully acknowledged. We thank Mr. Ronald Robinson of the Dow Corning Corporation for providing the mass spectra.

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Preparation and Vaporization Thermodynamics of Europium Oxide Bromides

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Abstract: Orthorhombic trieuropium tetraoxide monobromide, Eu_3O_4Br, ($a = 11.98 \pm 0.03$, $b = 10.36 \pm 0.02$, $c = 5.92 \pm 0.01$ Å); tetragonal europium monoxide monobromide, EuOBr, ($a = 3.926 \pm 0.003$, $c = 8.019 \pm 0.008$ Å); and hexagonal trieuropium monoxide tetrabromide, Eu_3OBr_4 ($a = 9.825 \pm 0.004$, $c = 7.510 \pm 0.003$ Å) have been prepared and their incongruent vaporization reactions investigated. Single-crystal X-ray diffraction data for Eu_3O_4Br are consistent with space group Pmnm or $Pmn2_1$. Values of $\Delta H°_{1399} = 129._0 \pm 1._1$ kcal/gram formula weight and $\Delta S°_{1399} = 50.8_1 \pm 0.8_1$ eu were obtained from target-collection Knudsen effusion measurements of the equilibrium dibromide pressure according to the reaction $3Eu_3O_4Br(s) \rightarrow 4Eu_2O_3(s, \text{monoclinic}) + EuBr_2(g) + Br(g)$. For $Eu_3O_4Br(s)$ $\Delta H_f°_{298} = -597._7 \pm 5._1$ kcal/gram formula weight, $\Delta G_f°_{298} = -565._0 \pm 5._1$ kcal/gram formula weight, and $\Delta S°_{298} = 64._5 \pm 3._1$ eu. Estimated thermodynamic data are presented for EuOBr ($\Delta H_f°_{298} = 203._3 \pm 6._5$ kcal/gram formula weight).

Although structural data for lanthanide monoxide monobromides (LnOBr) were reported by Zachariasen[2] in 1949, lanthanide–oxygen–bromine systems have been examined only recently. The thermogravimetric study of Zolotov and Mayer[3] indicated that the monoxide monobromides (LnOBr) were the only phases observed when Ln = La–Eu, but that an additional phase, $LnBr_3 \cdot LnOBr$, *i.e.*, Ln_2OBr_4, was present for the heavier analogs (Gd–Lu). Baernighausen, *et al.*,[4] confirmed the existence of the tetragonal, PbFCl-type monoxide monobromides and reported preparation of orthorhombic trilanthanide tetraoxide monobromides, Ln_3O_4Br (Ln = Sm, Eu, Yb). More recently Nd_3O_4Br has been reported.[5]

Thermodynamic data are not available for any of the europium–oxygen–bromine phases—the phase diagram has not been examined thoroughly—even though this is the best characterized lanthanide system. The preparative and thermodynamic data for both europium monoxide[6] and europium dibromide[7,8] suggest also that oxide bromides of Eu(II) should be stable. This work was initiated to examine the decomposition behavior of selected Eu–O–Br phases, to determine their thermodynamic stability, and to characterize more completely the ternary phase diagram.

Experimental Section

Samples of EuOBr were obtained only by direct bromination of the sesquioxide. A continuous helium flow which swept through a liquid bromine (technical grade, Dow Chemical Co., Midland, Mich.) reservoir carried the halogen vapor through a heated quartz

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