red spectrum in carbon disulfide solution showed an absorption band at 9.5 μ characteristic of a Si–O–Si linkage. This, together with the analytical data, indicate the compound to be 5,5′-oxybis-[5-phenyldibenzosilole]. Purification of the remaining crude product by crystallization could not be achieved.

Anal. Calcd. for $C_{36}H_{26}OSi_2$: C, 81.48; H, 4.94; Si, 10.57. Found: C, 81.26; H, 5.20; Si, 10.60, 10.57.

Reaction of 2,2′-Biphenylenedilithium with Hexachlorodisilane.—Three hundred and thirty milliliters of an ethereal solution containing 0.097 mole of 2,2′-biphenylenedilithium[7] was added, during 1.75 hours, to a stirred solution of 11.5 g. (0.043 mole) of hexachlorodisilane in 150 ml. of ether. The mixture was worked up in a manner similar to that described for 5-chloro-5-*n*-dodecyldibenzosilole except for using benzene instead of petroleum ether (b.p. 60–70°).[3a] Concentration and cooling of the benzene solution yielded 2.86 g. of crystals which, when crystallized from ethyl acetate, melted at 230–231° and showed no depression in melting point when admixed with an authentic sample of 5,5′-spirobi-[dibenzosilole] (II). From the mother liquor was obtained an additional 1.62 g. of II. Distillation of the remaining benzene left a residue which was sublimed at 130° (17 mm.) to give 1.75 g. of biphenyl, identified by mixed melting point. The residue was refluxed in acetone to give 7.25 g. of insoluble material which did not melt below 530°. Concentration of the acetone filtrate gave another 1.22 g. of II, m.p. 225–227°. The total yield of II was 5.70 g. (20% based on hexachlorodisilane).

An ethereal solution containing 4.69 g. of the residue obtained after removal of the benzene was treated with methyllithium. Work-up of the organic layer after hydrolysis yielded a viscous oil which could not be purified.

Reaction of Lithium with 5,5′-Dimethyl-5,5′-bi-[dibenzosilole].—Two grams (0.005 mole) of 5,5′-dimethyl-5,5′-bi-[dibenzosilole], 1.15 g. (0.166 g. atom) of finely cut lithium wire and 30 ml. of tetrahydrofuran were stirred at room temperature for 4 hours, after which the excess lithium was filtered off. To the resulting green mixture was added 1.5 g. (0.012 mole) of freshly distilled dimethyl sulfate dissolved in 10 ml. of tetrahydrofuran. The mixture was hydrolyzed with water, diethyl ether was added, and the organic layer was worked up in the usual manner. The crude product was distilled to give 0.2 g. of forerun followed by 1.15 g. (54%) of 5,5-dimethyldibenzosilole, b.p. 87° (0.005 mm.), which crystallized on cooling and melted at 55–57°. The melting point was undepressed when admixed with an authentic sample.[3]

Reaction of Lithium with 5,5-Dimethyldibenzosilole.—A mixture of 3.1 g. (0.0148 mole) of 5,5-dimethyldibenzosilole, 0.54 g. (0.072 g. atom) of finely cut lithium wire, 10 ml. of diethyl ether and 10 ml. of tetrahydrofuran was stirred at room temperature for 4.3 hours. The dark green mixture, which exhibited a positive Color Test I,[10] was hydrolyzed with water. The organic layer was separated and worked up in the usual manner. The residue was crystallized from methanol to give 1.60 g. of 5,5-dimethyldibenzosilole, m.p. 55–57°, identified by mixed melting point and infrared analysis. The solvent was evaporated from the filtrate and the residue was sublimed *in vacuo* to give an additional 0.35 g. of starting material, m.p. 53–55°, total yield 1.85 g. (60%). No reduction product was detected.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. The authors are also grateful to the Institute for Atomic Research, Iowa State College, and Mr. E. Miller Layton for assistance in the infrared determinations.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Silicon and Organosilicon Derivatives of Acetylacetone

BY ROBERT WEST

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Silicon and organosilicon derivatives of acetylacetone have been prepared and their structures have been investigated, principally by means of infrared spectroscopy. Chelated structures (I and II below) are proposed for the unsubstituted derivative $SiA_3Cl\cdot HCl$ (A = acetylacetonate group)[1] and also for monoalkyl compounds of the type $RSiA_2Cl$. The dialkylsilyl and trialkylsilyl acetylacetonates have open-chain, O-silylated structures such as III. The reasons for these structural differences are discussed.

Organometallic enolates generally are little-known, and no organosilicon derivatives of β-diketones are described in the literature.[2] This paper reports the synthesis of a series of organosilicon acetylacetonates and a study of their structure by means of infrared spectroscopy in the sodium chloride region. The unsubstituted silicon derivative of acetylacetone (HA)[1] was first prepared in 1903 by Dilthey[7,8] who found the product resulting from the reaction of $SiCl_4$ and HA to have the empirical formula $C_{15}H_{22}O_6SiCl_2$. Dilthey proposed for this compound a novel structure, $(SiA_3)^+Cl^-\cdot HCl$, containing a positively charged siliconium ion in which the silicon is chelated by 3 acetylacetonate groups. Dilthey prepared a number of derivatives of the tris-(2,4-pentanediono)-siliconium ion containing other anions, and proved the structure as well as possible using the techniques of his time. We have examined the infrared spectrum of $(SiA_3)^+Cl^-\cdot HCl$ and, as will be shown below, we find that the observed absorption bands confirm the unusual structure proposed by Dilthey.

The silyl derivatives of acetylacetone were prepared by three different general reactions: the direct reaction of a chlorosilane with acetylacetone in an inert solvent (A), a similar reaction assisted by the presence of the base pyridine (B) and the metathetical reaction between a chlorosilane and sodium acetylacetonate (C). Method A was used for the preparation of acetylacetonates of $SiCl_4$ and

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[1] The symbol A will be used to represent the acetylacetonate group, $C_5H_7O_2-$, throughout the remainder of this paper.

[2] The trimethylsilyl and triethylsilyl derivatives of ethylacetoacetate are known[3,4]; their structures are controversial.[3-6] The structures of these compounds will be discussed in a forthcoming paper.

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[7] W. Dilthey, *Ber.*, **36**, 923 (1903); *Ann.*, **344**, 300 (1906).

[8] A. Rosenheim, W. Loewenstamm and L. Singer, *Ber.*, **36**, 1833 (1903).

$$-\mathrm{SiCl} + \mathrm{HA} \longrightarrow -\mathrm{SiA} + \mathrm{HCl} \qquad \text{(A)}$$

$$-\mathrm{SiCl} + \mathrm{HA} + \mathrm{C_5H_5N} \longrightarrow -\mathrm{SiA} + \mathrm{C_5H_5NH^+Cl^-} \qquad \text{(B)}$$

$$-\mathrm{SiCl} + \mathrm{Na^+A^-} \longrightarrow -\mathrm{SiA} + \mathrm{Na^+Cl^-} \qquad \text{(C)}$$

alkyltrichlorosilanes. Methods B and C were both successful for the preparation of derivatives of the less reactive dialkyl and trialkylchlorosilanes, but method B generally was used.

Experimental

Materials.—The chlorosilanes were research grade chemicals obtained from the Dow-Corning Corporation. They were used without further purification. Eastman Kodak Co. white label acetylacetone was used after redistillation *in vacuo.*

Infrared Spectra.—Absorption spectra in the 650–5000 cm.$^{-1}$ region were obtained using a Baird model S automatic recording infrared spectrophotometer with sodium chloride prism. Liquids were studied as very thin liquid films pressed between sodium chloride plates, and solids were investigated as mulls in Stanolind white petroleum oil. In addition, all of the more stable compounds were observed in the 1500–1800 cm.$^{-1}$ region in dilute solution in chloroform. Observed spectral bands in the 1500–1800 and 950–1050 cm.$^{-1}$ regions are listed in Table I, and absorption in the 1500–1800 cm.$^{-1}$ region for some of the compounds is also shown in Fig. 1. Band positions are believed to be correct to within ±8 cm.$^{-1}$.

Tris-(2,4-pentanediono)-siliconium chloride 1-hydrogen chloride ($\mathrm{SiA_3Cl{\cdot}HCl}$) was prepared according to the method of Dilthey, by adding a solution of silicon tetrachloride in chloroform to a solution of acetylacetone in the same solvent. The solid product was precipitated by the addition of ether and recrystallized from a mixture of chloroform and ether. The compound was obtained thereby as a fine white crystalline powder melting with decomposition at 170–174°. The substance was soluble in water and alcohols as well as in chloroform, but insoluble in ether, hydrocarbons and carbon tetrachloride. The material is quite hygroscopic but is stable for months when stored out of contact with atmospheric moisture. Solution in water takes place without pronounced evolution of heat; this fact is in contrast to the behavior of compounds containing a Si–Cl bond. All of the chlorine can be titrated immediately with $\mathrm{AgNO_3}$ solution. As Dilthey observed,[2] the hydrolysis of acetylacetonate groups is slow. The freshly-prepared aqueous solution of the compound gives no immediate color when $\mathrm{FeCl_3}$ solution is added. An aqueous solution which has been allowed to stand for ten minutes gives a faint red color with $\mathrm{FeCl_3}$, while an aqueous solution aged for two hours or more gives an intense red color when $\mathrm{FeCl_3}$ is added.

Anal. Calcd. for $\mathrm{C_{15}H_{22}O_6SiCl_2}$: C, 45.3; H, 5.6; Cl, 18.1; Si, 7.1. Found: C, 44.9; H, 6.0; Cl, 17.5; Si, 7.0.

Some HCl can be removed from the compound under vacuum. A sample evacuated to 0.1 mm. overnight gave a chloride analysis corresponding to $\mathrm{SiA_3Cl{\cdot}0.5\ HCl}$. The compound now did not melt, but decomposed gradually above 200°. (The melting point observed for $\mathrm{SiA_3Cl{\cdot}HCl}$ is highly dependent on both HCl and moisture content.)

Methyl Bis-(2,4-pentanediono)-silicon Chloride [$\mathrm{CH_3SiA_2Cl}$].—To a large test-tube protected from atmospheric moisture and containing 10 ml. of anhydrous ether was added 2.0 g. (0.020 mole) of acetylacetone and 2.0 ml. (0.022 mole) of trimethylchlorosilane. The liquids were mixed and allowed to stand for five minutes, during which time the solution became slightly warm and crystallization of the product commenced. The ether was then evaporated under vacuum. The colorless solid product which remained was freed from any residual acetylacetone or trimethylchlorosilane by pumping under high vacuum for an hour. The yield was 2.6 g., 96%.

The compound decomposes on storage, turning brown in a few hours and undergoing complete decomposition in two days. Decomposition takes place even at −70°, although more slowly. The solid undergoes instantaneous and vigorous hydrolysis in water, and rapidly absorbs moisture when exposed to the air. Combustion analyses of this compound and the analogous phenyl compound for carbon were somewhat low, probably because of unavoidable decomposition and hydrolysis during handling of the compounds.

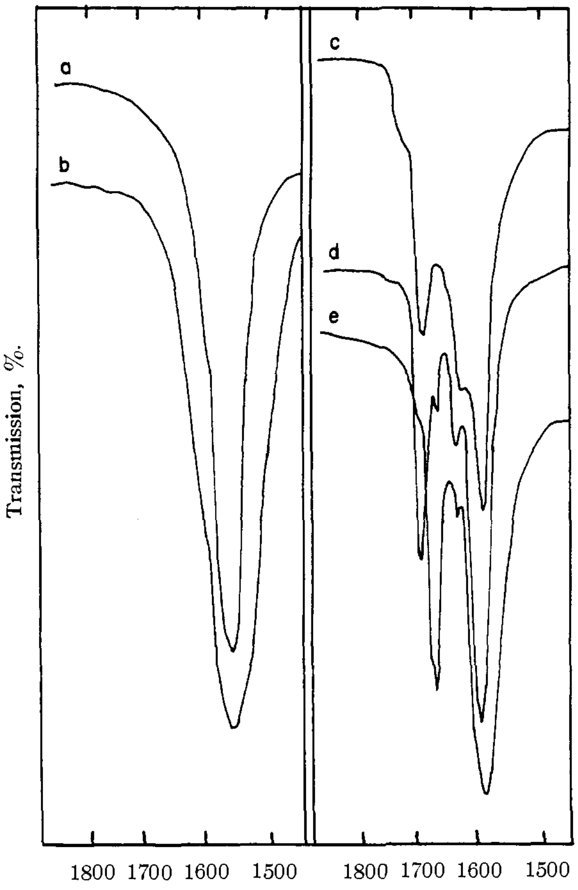


Fig. 1.—Infrared absorption of some representative acetylacetonates in the 1500–1800 cm.$^{-1}$ region, displaced for clarity: a, $\mathrm{SiA_3Cl{\cdot}HCl}$, 5% in $\mathrm{CHCl_3}$; b, $\mathrm{C_6H_5SiA_2Cl}$, Nujol mull; c, $\mathrm{(CH_3)_2SiA_2}$, thin liquid film; d, $\mathrm{(CH_3)_3SiA}$, 5% in $\mathrm{CHCl_3}$; e, 2-ethoxy-2-pentene-4-one, thin liquid film.

Anal. Calcd. for $\mathrm{C_{11}H_{17}O_4SiCl}$: C, 46.0; H, 6.1; Cl, 12.8. Found: C, 44.1; H, 6.0; Cl, 12.6.

The approximate ratio of hydrolyzable chlorine to acetylacetone in the compound was determined in the following way: A sample of the substance was added to distilled water, and brought to 100° to ensure complete hydrolysis of acetylacetonate groups. The cooled solution was then titrated with standard NaOH using a *p*H meter, first to an end-point at *p*H 6 to determine HCl, and then to a rather indefinite end-point at *p*H 10 to determine acetylacetone. The ratio Cl: acetylacetone so determined was 1:1.9.

Phenyl bis-(2,4-pentanediono)-silicon chloride [$\mathrm{C_6H_5SiA_2Cl}$] was prepared by the method used for the methyl analog. Like the methyl compound, it is a colorless crystalline solid which reacts immediately with water and decomposes in only a few hours at room temperature. The ratio Cl: acetylacetone, determined by the method outlined above, was found to be 1:1.9.

Anal. Calcd. for $\mathrm{C_{16}H_{19}O_4SiCl}$: C, 56.7; H, 5.5; Cl, 10.4. Found: C, 54.8; H, 5.6; Cl, 10.5.

Dimethylsilyl Bis-(2-oxy-2-pentene-4-one) [$\mathrm{(CH_3)_2SiA_2}$].—A mixture of 200 ml. of pentane, 61 g. (0.6 mole) of acetylacetone and 48 g. (0.6 mole) of pyridine, freshly distilled from barium oxide, was cooled in an ice-bath and 39 g. (0.3 mole) of dimethyldichlorosilane, diluted with 50 ml. of pentane, was added dropwise with stirring. After the addition was complete the mixture was allowed to warm to 30° and kept at this temperature with stirring for 30 minutes. The precipitate of pyridinium chloride was filtered quickly and washed with pentane. The amount of pyridinium salt recovered was 60 g. (85%). The filtrate and washings were then evaporated at 0° under vacuum, and the residue was fractionated under high vacuum. The crude product was obtained as a yellow liquid boiling at 128–134° at 0.04 mm. The crude yield was only 8 g., or 11%. The material darkens during the distillation, and about 60 g. of dark, apparently polymeric residue is left behind in the still pot. Refractionation gave about 4 g. of pure product as a pale yellow oil, b.p. 125–128° at 0.03 mm., $n^{25}D$ 1.4650, d^{25}_4 1.016. The liquid slowly turned dark when stored in glass at room temperature.

Anal. Calcd. for $C_{12}H_{20}O_4Si$: C, 56.2; H, 7.9; mol. ref.,[9] 68.6. Found: C, 55.6; H, 7.6; mol. ref., 69.9.

2-Trimethylsiloxy-2-pentene-4-one [$(CH_3)_3SiA$]. **Method B.**—A mixture of 40 g. (0.5 mole) of pyridine, 51 g. (0.5 mole) of acetylacetone and 200 ml. of petroleum ether, b.p. 30–60°, was treated dropwise with trimethylchlorosilane (54 g., 0.5 mole). The mixture was then refluxed and stirred for five hours and allowed to stand overnight. The solution was filtered to remove pyridinium chloride, 38 g. (67%). The filtrate and washings were evaporated under reduced pressure, and the residue was fractionally distilled, yielding 40 g. (46%) of colorless liquid product, b.p. 66–68° (4 mm.). The compound had $n^{25}D$ 1.4546 and d^{25}_4 0.912. It was stable when sealed in glass, but underwent hydrolysis readily in contact with moisture, giving hexamethyldisiloxane and 2,4-pentanedione as products.

Method C.—Sodium sand[3] was prepared from 4.6 g. (0.2 g.-atom) of sodium metal in 200 ml. of toluene. A solution of 20 g. (0.2 mole) of acetylacetone in 80 ml. of toluene was added slowly with stirring. The reaction mixture was warmed to 45° and stirred for two hours to complete the formation of the sodium salt. After the mixture had been cooled to room temperature a solution of 22 g. (0.2 mole) of trimethylchlorosilane in 50 ml. of toluene was added, and finally the mixture was warmed to 100° and stirred for 4 hours.

The mixture was then cooled and filtered with suction. The sodium chloride was washed with toluene, and the toluene was distilled from the filtrate at room temperature and about 30 mm. pressure. The residue was distilled fractionally to give 21 g. (62%) of the desired $(CH)_3SiA$.

Anal. Calcd. for $C_8H_{16}O_2Si$: C, 55.8; H, 9.4; mol. ref., 49.3. Found: C, 55.4; H, 9.0; mol. ref., 51.2.

2-Triethylsiloxy-2-pentene-4-one [$(C_2H_5)_3SiA$] was prepared by method B given above for $(CH_3)_3SiA$. The yield of the triethylsiloxy compound was 53%, boiling at 96–97° (2.1 mm.). The product was a colorless liquid with $n^{25}D$ 1.4641 and d^{25}_4 0.910.

Anal. Calcd. for $C_{11}H_{22}O_2Si$: C, 61.6; H, 10.4; mol. ref., 63.2. Found: C, 61.6; H, 10.4; mol. ref., 65.0.

2-Trimethylsiloxy-3-methyl-2-pentene-4-one.—3-Methyl-2,4-pentanedione was prepared from potassium acetylacetonate and excess methyl iodide in a steel pressure vessel at 150°, following the directions given by Morgan and Thomason for the 3-propyl compound.[10] After purification through the potassium salt, 3-methyl-2,4-pentanedione was obtained in 31% yield. The reaction with trimethylchlorosilane was carried out by method B above, but the yield was lower (16%). The product was also a colorless liquid, b.p. 89–91° (8 mm.), $n^{25}D$ 1.4563 and d^{25}_4 0.930. The liquid slowly turned dark on standing.

Anal. Calcd. for $C_9H_{18}O_2Si$: C, 57.9; H, 9.8; mol. ref., 53.9. Found: C, 57.9; H, 9.7; mol. ref., 54.5

2-Ethoxy-2-pentene-4-one was prepared from silver acetylacetonate and ethyl iodide at 20° according to the method of Curtiss.[11] The C-alkylated compound obtained as a by-product was removed by extraction from ether solution into aqueous alkali. The ether solution was dried and distilled to give a total of 24 g. of the pure enol ether b.p. 71–72° (15 mm.), representing a 30% yield. The compound is a liquid, $n^{25}D$ 1.4612, d^{25}_4 0.941. The product has a pleasant pungent odor. Initially it is colorless but it soon turns green and then brown as it undergoes decomposition.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4; mol. ref., 36.0. Found: C, 66.1; H, 9.5; mol. ref., 37.4.

TABLE I

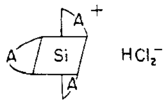
INFRARED ABSORPTION BANDS[a]

Compound	1500–1800 cm.$^{-1}$			950–1050 cm.$^{-1}$	
$SiA_3{}^+Cl^-\cdot HCl$			1555	1023	
CH_3SiA_2Cl			1550	1033	
$C_6H_5SiA_2Cl$			1553	1047	
$(CH_3)_2SiA_2$	1669	(1620) 1595		1030	
$(CH_3)_3SiA$	1678 (1658)	(1620) 1592		1025	(982)
$(C_2H_5)_3SiA$	1681	(1620) 1592		1010	(1033)
$(CH_3)_3Si(C_6H_9O_2)$[12]	1672 (1640)	(1610) 1587		994	
C_2H_5A[13]	1672	(1626) 1580			

[a] Weak bands or shoulders are given in parentheses.

Infrared Spectra and Structure.—$SiA_3Cl\cdot HCl$ has no infrared absorption in the usual carbonyl region near 1700 cm.$^{-1}$, and instead has a single very strong and broad absorption band at 1555 cm.$^{-1}$. This intensification and very large shift of the C—O absorption band from its usual position can only be accounted for by assuming that the carbonyl oxygens are forming strong complexes with some acidic site, which must in this case be the silicon atom. This type of absorption is found in metal chelates, all of which have one or two strong bands in the 1500–1600 cm.$^{-1}$ region.[14] We therefore assign to this compound structure I identical with that proposed by Dilthey[2] in that the three acetylacetonate groups are chelated about a siliconium ion, occupying six $3s3p^33d^2$ hybrid orbitals octahedrally distributed about the silicon. None of the chemical properties described in the Experimental section are inconsistent with this formulation.

The additional molecule of HCl present in the compound seems too firmly held to be accounted for without invoking chemical bonding of some sort. We suggest that the HCl is present as hydrogen dichloride anions, HCl_2^-, which are known to form stable salts with large, weakly polarizing cations.[15]



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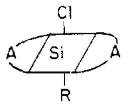

II

CH_3SiA_2Cl and $C_6H_5SiA_2Cl$, like $SiA_3{}^+HCl_2{}^-$, have very strong infrared absorption bands near 1550 cm.$^{-1}$ and no other absorption in the 1500–1800 cm.$^{-1}$ region. The two acetylacetonate groups present per silicon atom must be chelated, occupying four of the six coördination positions on the silicon atom. We therefore assign to these compounds a structure in which the organic group and

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[10] G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, **125**, 754 (1924).

[11] R. S. Curtiss, *Am. Chem. J.*, **17**, 435 (1895).

[12] 2-Trimethylsiloxy-3-methyl-2-pentene-4-one.

[13] 2-Ethoxy-2-pentene-4-one.

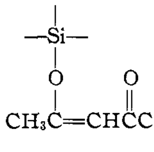
[14] J. Lecomte, *Disc. Faraday Soc.*, **9**, 125 (1950); R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958); L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co., London, 1954, p. 126.

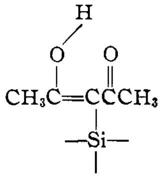
[15] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, THIS JOURNAL, **76**, 4046 (1954); R. West, *ibid.*, **79**, 4568 (1957).

the chlorine each take up one of the remaining octahedral valence positions; we believe that these compounds are the first known hexacoördinate organosilicon compounds. One of the three isomeric structures available to these compounds is shown as II above.

Dimethylsilyl and Trialkylsilyl Acetylacetonates.—All of these compounds are liquids with two strong bands in the 1500–1800 cm.$^{-1}$ region, at about 1670 and 1590 cm.$^{-1}$. The first of these is easily assigned since it is in just the proper position for a conjugated (but not chelated) carbonyl group.[16] Following Rasmussen, Tunnicliff and Brattain,[17] we assign the 1590 cm.$^{-1}$ band to the C=C vibration, enhanced in intensity and shifted to lower frequency both by conjugation and by the presence of an electronegative (siloxy) substituent group. These assignments are strengthened by comparison with the spectrum of the enol ether of acetylacetone, 2-ethoxy-2-pentene-4-one (Table I and Fig. 1). The infrared absorption of this compound in the 1500–1800 cm.$^{-1}$ region is virtually identical with that of the silicon compounds.

Two possible structures (III and IV) are compatible with the observed infrared absorption for the silicon compounds. Of these the C-silylated structure IV can be eliminated on the basis of the following evidence: 1. The compounds in question do not contain a hydroxylic hydrogen atom, as is shown by the infrared spectrum, the n.m.r. spectrum, and the fact that the compounds do not give methane on treatment with CH_3MgI. 2. The compounds have a strong infrared band near 1020 cm.$^{-1}$, attributable to Si–O vibration.[18] 3. The trimethylsilyl derivative of 3-methyl-2,4-pentanedione would, if C-silylated, be required to have the structure of an *unconjugated* β-diketone, whereas this compound has infrared absorption in the 1500–1800 cm.$^{-1}$ region similar to that of the other trialkylsilyl compounds. The dialkyl and trialkylsilyl acetylacetonates are therefore assigned the enol ether structure III.


III


IV

The molar refraction of these enol ethers is higher than the calculated amount by 0.6 to 1.9 ml. This exaltation of refraction is typical of conjugated ketones, and is of the same order of magnitude as that observed for 2-ethoxy-2-pentene-4-one (1.4 ml.).

Discussion

From the foregoing it appears that the structure of the organosilicon acetylacetonates changes from chelated in $SiA_3Cl{\cdot}HCl$, CH_3SiA_2Cl and $C_6H_5A_2Cl$, to open-chain in the dimethyl and trialkylsilyl compounds. The reasons for this change of structure type are worthy of consideration. Steric hindrance cannot explain the lack of chelation in $(CH_3)_2SiA_2$, since the steric requirement of a chlorine atom is approximately equal to that of a methyl group, and the compound CH_3SiA_2Cl is chelated. The presence of the electronegative chlorine atom on the silicon apparently increases the acidity of the silicon, by withdrawal of electrons, sufficiently so that chelation can take place in the $RSiA_2Cl$ compounds. In $SiA_3Cl{\cdot}HCl$, the acetylacetonate groups themselves must be sufficiently electron-withdrawing so that the compound adopts a chelated structure.

Since the coördination of a nucleophilic group into a vacant *d* orbital of the silicon atom appears to be the first step in the rapid hydrolysis of halosilanes,[19] it might be expected that hexacoördinate compounds $RSiA_2Cl$ would be slow to hydrolyze. In fact, the Si–Cl bonds in these compounds hydrolyze instantaneously and exothermically in water. Perhaps the solvolysis of these compounds may be assisted by prior dissociation into $RSiA_2^+$ and Cl^- ions. The low thermal stability of the monoalkyl chelates, compared to $SiA_3Cl{\cdot}HCl$, is also remarkable.

The acetylacetonate group is an ambident anion, which can undergo alkylation either at the oxygens or at the central carbon atom. The recently-proposed rule of Kornblum[20] states that the alkylation of ambident anions takes place at the more negative atom in S$_N$1 reactions, and at the more positive atom in S$_N$2 reactions. The mechanism of the silylation reaction is not known, but it seems very unlikely that it takes place by an S$_N$1 mechanism, involving dissociation into R_3Si^+ and Cl^- ions prior to the attack by A^-. Such S$_N$1 reactions are unknown in organosilicon chemistry; the nucleophilic substitution reactions occurring at silicon whose mechanisms are known all appear to follow a bimolecular mechanism, which may involve a pentacovalent intermediate.[19,21] If the reaction of chlorosilanes with acetylacetone follows a similar mechanism, it represents an apparent violation of Kornblum's rule, since the silicon always becomes attached to the more electronegative oxygen atom. Further examples of the reaction of organosilicon halides with ambident anions are now being investigated.

Acknowledgments.—The author is indebted to Miss Peggy Pamela Hoffman and Mrs. Leonard Suffredini for assistance in preparing two of the compounds herein described, and to Dr. Reed Riley for much helpful discussion of theoretical points.

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