

Silicon(IV) Compounds Containing 1,3-Diketo Ligands

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Abstract: A series of tetracarboxysilanes has been found to undergo a general reaction with various 1,3-diketones to yield neutral hexacoordinated silicon chelate derivatives. An investigation of the chemical reactivity of bis(2,4-pentanediono)diacetatosilicon(IV) showed that this compound undergoes unidentate and bidentate ligand exchange under suitable conditions while maintaining the octahedral structure.

A recent communication from this laboratory reported the preparation of bis(2,4-pentanediono)diacetatosilicon(IV).³ The present paper describes further results of the investigation of the chemical reactivity of this compound. Furthermore, the preparation of a number of other representative derivatives belonging to this new class of hexacoordinate silicon chelates having 1,3-diketo ligands is reported.

Silicon acetylacetonates were first reported by Dilthey⁴ who prepared a number of derivatives of the bis(2,4-pentanediono)siliconium ion, $(C_5H_7O_2)_3Si^+$, formed by treating silicon tetrachloride with acetylacetone. Salts such as $(C_5H_7O_2)_3Si^+ \cdot HCl_2^-$ and $(C_5H_7O_2)_3Si^+ \cdot FeCl_4^-$

The silane carboxylate starting materials were prepared by several methods. Tetraacetoxysilane was obtained by treatment of silicon tetrachloride with *t*-butyl acetate,⁸ tetrapropionoxysilane was prepared by treatment of silicon tetrachloride with sodium propionate,⁹ and tetrabenzoyloxysilane, tetra-*n*-butyroxysilane, and tetra(chloroacetoxy)silane were prepared by treatment of silicon tetrachloride with the corresponding anhydride.¹⁰

Results and Discussion

The silicon chelate derivatives were prepared by the rapid addition of selected 1,3-diketones to a chloroform

Table I. Infrared Absorption Bands (Frequency, cm⁻¹)

Compd ^a	C=O in carbonyl group	C—C stretch	C—O stretch	Si—O—C stretch	C—H out of plane bending	Ring deformation	C—CH ₃ and Si—O
1	1750	1575	1550	1050	830	693	665
2	1709	1565	1550	1043	805
3 ^b	1720	1575	1550	1042	...	693	655
3 ^c	1720	1580	1550	1040	...	690	650
4	1725	1570	1550	1040	...	710	...
5	1700	1580	1550	1045	850	700	667
6	1700	1550	1290	1020	822	738	...
7 ^d	1680	1535	1400	1025	...	710	...
7 ^e	1680	1530	1400	1030	...	723	...

^a The names of the compounds listed above are (1) bis(2,4-pentanediono)diacetatosilicon(IV), (2) bis(2,4-pentanediono)di-*n*-propionatosilicon(IV), (3) bis(2,4-pentanediono)di-*n*-propionatosilicon(IV), (4) bis(2,4-pentanediono)di(chloroacetato)silicon(IV), (5) bis(2,4-pentanediono)dibenzoylatosilicon(IV), (6) bis(4,4,4-trifluoro)-1-(2-thenyl)-1,3-butanediono)diacetatosilicon(IV), (7) bis(1,3-diphenyl-1,3-propanediono)diacetatosilicon(IV). ^b Prepared from tetra-*n*-butoxysilane and acetylacetone. ^c Prepared from chelate 1 and sodium butanate. ^d Prepared from dibenzoylmethane and tetracetoxysilane. ^e Prepared from chelate 1 and dibenzoylmethane.

were isolated and characterized. The assigned octahedral structure for this class of chelates was later confirmed by infrared analysis,⁵ partial resolution,⁶ and more recently by nuclear magnetic resonance data.⁷

It was found in the present work that use of organocarboxysilanes in place of the previously employed silicon tetrachloride leads to the formation of a new class of hexacoordinate acetylacetonate silicon derivatives. The general structure of the new silicon chelates is illustrated in Figure 1.

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(2) Abstracted in part from a dissertation submitted by R. R. Luongo in partial fulfillment of the requirements for the Ph.D. degree in chemistry, June 1965.

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slurry containing the silane carboxylate. The derivatives prepared are summarized in Table I. The majority of these materials are stable when stored under an inert atmosphere.

Previous work in this area using silicon tetrachloride had led to the formation of the ionic trisbidentate materials.⁴⁻⁶ To establish that the new chelates reported in the present work were nonionic, bis(2,4-pentanediono)diacetatosilicon(IV) was treated with ferric chloride in chloroform solvent under conditions similar to those employed by Dilthey.⁴ No reaction was detected, either by a rise in temperature or by the precipitation of an iron salt.

Spectral data have been used extensively in the metal

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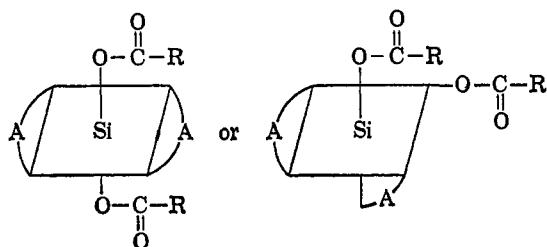


Figure 1. General structure in silicon chelates: A may be 2,4-pentanediono, 1,3-diphenyl-1,3-propanediono, or 4,4,4-trifluoro-1-(2-thenyl)-1,3-butanediono; R may be CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, ClCH_2 , or C_6H_5 .

acetylacetonate systems to establish the chelate structure of these materials. Nakamoto has compiled much of this data.¹¹ The key assignments in Table I are made based on the infrared spectra of the chelates. All of the bands except those in the 1700-cm^{-1} region are usually observed for metal acetylacetonates.¹¹⁻¹³ The intensification and very large shift of the carbonyl frequency from 1625 cm^{-1} observed in acetylacetonate to $1540\text{-}1550\text{ cm}^{-1}$ in compounds 1-5 is typical of the metal acetylacetonates. The carbonyl shift in compound 7 is more difficult to ascertain. Dibenzoylmethane, unlike acetylacetonate, shows a strong carbonyl absorption in the $1590\text{-}1540\text{-cm}^{-1}$ region. Hence, although the product formed from this 1,3-diketone show absorption in the region generally characteristic of chelate formation, it is difficult from infrared studies to conclude that a chelate is produced based on a carbonyl shift. It has been noted that the $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{O}$ absorption bands for bis(1,3-diphenyl-1,3-propanediono)copper(II) occurred at 1524 and 1391 cm^{-1} , respectively.¹⁴ These assignments would agree with the observed assignments for compound 7.

The shift in carbonyl absorption in 4,4,4-trifluoro-1-(2-thenyl)-1,3-butanedione from 1640 cm^{-1} , due to the enolic grouping, to 1550 cm^{-1} , was observed. It has been noted that various metal chelates prepared from this particular 1,3-diketone show their $\text{C}\equiv\text{O}$ absorption at $1570\text{-}1603\text{ cm}^{-1}$. Thus, the absorption at 1550 cm^{-1} is ascribed to $\text{C}\equiv\text{O}$ which is indicative of chelate formation.

Holm and Cotton have reported that the ultraviolet spectra of metal acetylacetonates are characterized by strong absorption in the $270\text{-}300\text{-m}\mu$ region and an extinction coefficient of greater than $20,000$ ($\text{l. mole}^{-1}\text{ cm}^{-1}$).¹⁵ The spectrum of compound 1 in chloroform solvent showed a λ_{max} of $279\text{ m}\mu$ and an extinction coefficient of $20,041$ ($\text{l. mole}^{-1}\text{ cm}^{-1}$). It had previously been noted that this increase in the extinction coefficient over that of acetylacetonate ($\lambda_{\text{max}} 10,600\text{ l. mole}^{-1}\text{ cm}^{-1}$), is typical for the metal acetylacetonate derivatives.

A preliminary investigation of the nuclear magnetic resonance spectrum of compound 1 indicates a typical metal acetylacetonate chelate structure. Further in-

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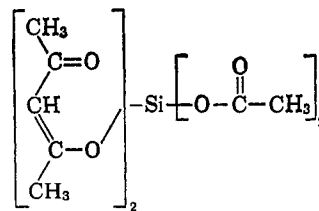


Figure 2. The diacetoxysilyl ester of the enolate of acetylacetonate.

vestigation on this aspect of these compounds is under way and will be published shortly.¹⁶

Further evidence to support the chelate structure of these materials was obtained by the isolation of an intermediate in the preparation of compound 1. It was found that the addition of the acetylacetonate to the tetraacetoxysilane at 5° resulted in the formation of a material having mp 150° dec. The infrared spectrum showed *no absorption* in the $1500\text{-}1600\text{-}$ or $650\text{-}700\text{-cm}^{-1}$ regions which are indicative of bidentate chelation of the acetylacetonate group to a metal atom. This material is postulated to be the diacetoxysilyl ester of the normal enolate of acetylacetonate (Figure 2). This compound having mp 150° dec was then heated under conditions which were first found to form the chelate 1 directly from the same reactants. Isolation and purification of the resulting product gave a material having an infrared absorption spectrum similar to that summarized for compound 1 in Table I.

Based on the above spectral and chemical evidence the structure shown in Figure 1 has been assigned to the subject chelate derivatives. Attempts to separate the possible *cis* and *trans* isomers and to resolve the former are under way. To date, the results have not been successful.

It was of interest to initiate an investigation of the reactions which these new species might undergo. It was therefore decided to determine whether unidentate and bidentate ligand exchange could be effected. Bidentate ligand exchange was carried out by treating chelate 1 with dibenzoylmethane in chloroform solvent. The infrared spectrum, elemental analysis, and the melting point of the resulting product confirmed the isolated material to be chelate 7. Chelate 7 had previously been prepared by treatment of tetraacetoxysilane with dibenzoylmethane. When an exchange was attempted with 4,4,4-trifluoro-1-(2-thenyl)-1,3-butanedione and chelate 1 in an attempt to prepare chelate 6 a color change in the reaction mixture occurred but no further evidence that a reaction had taken place could be detected. It is felt that the exchange involving dibenzoylmethane is facilitated by the extreme insolubility of chelate 7 in chloroform, thereby driving the reaction to completion.

To obtain further evidence that true ligand exchange had occurred, the product obtained from tetraacetoxysilane and dibenzoylmethane and the above bidentate ligand exchange product from chelate 1 and dibenzoylmethane were hydrolyzed under acid conditions. The recovered amount of dibenzoylmethane was in both cases greater than 90%. This substantiates that true ligand exchange did occur.

Monodentate exchange of the carboxyl units on chelate 1 was also investigated. Treatment of this

(16) This investigation is being undertaken by Dr. C. E. Holloway at the University of Western Ontario, Ontario, Canada.

chelate with sodium propionate and sodium butanate led to the formation of chelates 2 and 3, respectively. Comparison of the infrared spectra, elemental analysis, and melting point confirmed that these products were identical with those obtained by treatment of acetylacetone with the corresponding tetracarboxylsilanes.

The significance of the success of the exchange reactions lies in the fact that if the geometrical isomers of the chelates can be separated, and those of the *cis* isomer resolved, one has a system which would make it possible to undertake an investigation of the mechanism of these displacement reactions on hexacoordinated silicon. Furthermore, selected geometrical species may be useful for incorporation of hexacoordinated silicon chelates into polymeric systems.

Experimental Section

Spectroscopic Measurements. The infrared spectra were obtained by use of a Beckman IR-5 spectrophotometer using sodium chloride plates. Solid samples were run as Nujol mulls and liquids in sodium chloride liquid cells.

The ultraviolet spectra were obtained in chloroform solvent, using quartz cells. The extinction coefficient of bis(2,4-pentanedione)diacetatosilicon(IV) was determined from two different solutions.

Molecular Weight Measurements. Molecular weight determinations were carried out by the cryoscopic method, using redistilled bromoform or dibromoethylene as the solvent.

Analytical Methods. Sulfur was determined using a Schöniger oxygen flask.¹⁷ Nitrogen was determined using a micro-Kjeldahl technique.¹⁸ Chlorine was determined as the silver salt employing a gravimetric procedure.¹⁹ Silicon was determined by the method of Mihard.²⁰ Carbon and hydrogen were determined by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

General Reaction Conditions. All the reactions given below were carried out under a nitrogen atmosphere. The isolated products were stored in sealed vials which had previously been flushed with nitrogen. The melting points are uncorrected.

Tetraacetoxysilane. Tetraacetoxysilane was prepared by treatment of *n*-butyl acetate (20.8 g, 0.18 mole) with silicon tetrachloride (1.5 g, 0.04 mole) in a stoppered, 50-ml erlenmeyer flask. After allowing the solution to stand overnight, crystals of tetraacetoxysilane appeared. The product was collected by filtration under suction and washed with petroleum ether (bp 30–60°). Tetraacetoxysilane (8.9 g, 86%) was obtained having mp 107–110° (lit.⁹ mp 110°).

Anal. Calcd for C₈H₁₂O₈Si: sapon equiv, 66.0. Found: sapon equiv, 67.2.

Tetrapropionoxysilane. Dried sodium propionate (45.2 g, 0.47 mole) was dissolved in 100 ml of dried benzene and introduced into a three-necked flask fitted with a mechanical stirrer, dropping funnel, and condenser. To this, at room temperature, was added dropwise silicon tetrachloride (16 g, 0.19 mole) in 20 ml of dried benzene. Too rapid an addition resulted in a violent reaction. After the addition was completed the reaction mixture was heated at reflux temperature for a period of 3 hr. After allowing the system to cool, the benzene layer was tested for the presence of chlorides by withdrawing a small amount of solvent and treating this portion with silver nitrate solution. No precipitate of silver chloride formed. The reaction mixture was then filtered under suction and the solid was washed with 50 ml of fresh benzene. Sodium chloride (33.2 g) was collected. The filtrate and washings were combined and the benzene solvent was removed at room temperature under reduced pressure. A viscous, straw-colored liquid (22.6 g, 37%) remained.

Anal. Calcd for C₁₂H₂₀O₈Si: Si, 8.77. Found: Si, 9.18.

Tetra(*n*-butyloxy)silane. In a 50-ml, one-neck, round-bottom flask was placed 31.6 g (0.20 mole) of redistilled *n*-butyric anhydride followed by 8.3 g (0.049 mole) of redistilled silicon tetrachloride.

The flask with its contents was fitted to a microdistillation apparatus and then heated to reflux temperature. *n*-Butanoyl chloride (16.5 g, 80% yield) was obtained having bp 102° (lit.²¹ bp 102°).

The higher boiling residue was then removed having bp 190–194°. A suitable separation from unreacted *n*-butyric anhydride (bp 192–194°) could not be effected by this method. An infrared spectrum of the material indicated the presence of the anhydride. However, the crude material was of sufficient purity to be used for the preparation of the desired chelates.

Anal. Calcd for C₁₈H₂₆O₈Si: Si, 7.45. Found: Si, 6.43.

Tetra(chloroacetoxy)silane. In a 50-ml, one-neck round-bottom flask was placed monochloroacetic anhydride (25 g, 0.15 mole) and silicon tetrachloride (6.1 g, 0.035 mole). The flask with its contents was then fitted to a microdistillation apparatus and the temperature was raised to 110°. Chloroacetyl chloride, bp 104–105°, was obtained amounting to 14.1 g (86%). On cooling the high-boiling residue, a tan solid separated. This mixture was treated with 20 ml of dried benzene and filtered under suction. A sugary, white solid, (4.85 g), mp 135–140°, was obtained. Recrystallization from a benzene-ligroin mixture gave 3.5 g of a white, crystalline solid having mp 150° (lit.¹⁰ mp 154°).

Anal. Calcd for C₈H₈O₈Cl₄Si: Si, 6.94. Found: Si, 6.99.

Tetrabenzoyloxysilane. In a 50-ml, one-necked, round-bottom flask was placed benzoic anhydride (21.6 g, 0.096 mole) and silicon tetrachloride (4.1 g, 0.024 mole). After attachment of the flask to a microdistillation column, the mixture was heated to 100–110° for a period of 2 hr. After cooling, benzoyl chloride, 10.6 g (80%), was obtained at bp 59–60° (5.0 mm), *n*_D²⁰ 1.5520. The high-boiling residue on cooling solidified to give 11.7 g of a pale yellow, waxy solid, mp 67–70°. This material was recrystallized from a benzene-petroleum ether mixture and had mp 80–85° (lit.⁶ mp 85–90°).

Bis(2,4-pentanedione)diacetatosilicon(IV). In a dried, 100-ml flask fitted with a condenser, dropping funnel, thermometer, and magnetic stirrer was placed tetraacetoxysilane (8.54 g, 0.032 mole) and dried chloroform (12 ml). Redistilled acetylacetone (6.9 g, 0.069 mole) was then added rapidly to the slurry causing a temperature rise of 25 to 60°. After the addition was completed, the temperature was raised to 70–75° for a period of 2 hr with stirring. The reaction mixture was then cooled and filtered under suction in a nitrogen atmosphere. There was collected 12.2 g of a light yellow solid having a strong odor of acetic acid. It had mp 170–175° dec. Recrystallization of this material from a chloroform-petroleum ether mixture gave 5 g (45%) of white crystalline bis(2,4-pentanedione)diacetatosilicon(IV), mp 180–185° dec.

Anal. Calcd for C₁₄H₂₀O₈Si: C, 48.82; H, 5.58; Si, 8.16; equiv wt, 86.1; mol wt, 344. Found: C, 48.52; H, 5.98; Si, 8.19; equiv wt, 88.0; mol wt, 346.

The Diacetoxysilylbisolate of Acetylacetone. Acetylacetone was treated with tetraacetoxysilane in a 2.1 to 1 mole ratio. The same procedure employed for the preparation of bis(2,4-pentanedione)diacetatosilicon(IV) was used. However, the acetylacetone was slowly added dropwise to a slurry of the tetraacetoxysilane in chloroform at 0–5° and the temperature was not allowed to exceed 5° during the course of the addition. After the addition was completed, a white solid had formed. Stirring was continued at 0–5° for 15 min. A portion of the reaction product was then withdrawn, collected under suction, and washed with 15 ml of petroleum ether. This material had a melting point of 150° dec. The remainder of the reaction product was then heated to 70–75° for 1 hr. On cooling, the solid product was collected under suction. This material had mp 170–175° dec. The infrared spectra of the lower and higher melting materials were then compared. From the difference in the carbonyl absorption of the two spectra, the lower melting material was postulated to be the diacetoxysilylbisolate of acetylacetone.

Anal. Calcd for C₁₄H₂₀O₈Si: Si, 8.16; equiv wt, 86.1. Found: Si, 8.14; equiv wt, 89.3.

The spectrum of the higher melting material was similar to that of bis(2,4-pentanedione)diacetatosilicon(IV).

Bis(2,4-pentanedione)dipropionatosilicon(IV). The apparatus employed was similar to that previously described for the preparation of bis(2,4-pentanedione)diacetatosilicon(IV). To 5 g (0.016 mole) of tetrapropionoxysilane was added 7 ml of dried chloroform followed by the dropwise addition of acetylacetone (3.34 g, 0.033 mole). A temperature rise of 10° resulted upon mixing. After the addition was completed the reaction mixture was filtered under

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suction and petroleum ether added to the filtrate until it became cloudy. After standing in the refrigerator overnight there was collected 2.5 g (43%) of an intense yellow solid, mp 140–150° dec.

Anal. Calcd for $C_{16}H_{24}O_8Si$: Si, 7.56; equiv wt, 93.1; mol wt, 372.4. Found: Si, 7.59; equiv wt, 96.2; mol wt, 361.

Bis(2,4-pentanediono)di(*n*-butyrate)silicon(IV). To 10 g of crude tetra(*n*-butyroxysilane was introduced 10 ml of chloroform followed by the dropwise addition of acetylacetone (4 g, 0.04 mole). A temperature rise from 25 to 55° was noted during the course of addition. After the addition was completed, the temperature was raised to 70–72°. After 15 min a deep yellow color developed, after 30 min a yellow-red color formed, and after 1.5 hr a deep red-colored solution resulted. After cooling, the reaction mixture was filtered under suction and the filtrate was extracted three times with 20-ml portions of petroleum ether. Five grams (47%) of a deep red, viscous liquid having a strong odor of butyric acid was isolated. It was previously determined that *n*-butyric anhydride, acetylacetone, and tetra(*n*-butyroxysilane were infinitely soluble in petroleum ether. Thus, by extraction, unreacted materials were separated from the product. On standing, the red viscous product solidified giving a low-melting solid. It readily decomposed to a purple mass when exposed to the atmosphere and when stored in a sealed container under nitrogen, it decomposed in 1 to 2 days.

Anal. Calcd for $C_{18}H_{28}O_8Si$: Si, 7.02; equiv wt, 100.1; mol wt, 401. Found: Si, 6.17; equiv wt, 97.0; mol wt, 435.

Bis(2,4-pentanediono)di(chloroacetato)silicon(IV). To 3.5 g (0.009 mole) of tetra(chloroacetoxy)silane was added 5 ml of dried chloroform to form a slurry. Acetylacetone (1.87 g, 0.019 mole) was then added dropwise. This caused a heat rise from 31 to 46°. Solution was effected after the addition was completed. After 15 min at room temperature, a turbid system had formed. The temperature was then raised to 45–50° for a period of 2 hr. On cooling, the reaction mixture was filtered under suction and washed with ligroin giving 1 g (28%) of a white solid. This material yellowed at 155°, turned a dark yellow at 170°, and decomposed to a dark red liquid at 180–185°.

Anal. Calcd for $C_{14}H_{18}O_8SiCl_2$: Si, 6.80; Cl, 17.15; equiv wt, 103. Found: Si, 6.88; Cl, 17.1; equiv wt, 90.2.

Bis(2,4-pentanediono)dibenzoylato)silicon(IV). To a solution containing 9 g (0.018 mole) of tetrabenzoyloxysilane suspended in 2 ml of chloroform was added dropwise at room temperature, acetylacetone (3.77 g, 0.038 mole). During the course of the addition the reaction mixture assumed a yellow, chalky appearance. After the addition was completed, the temperature was raised to 50–60° for 2 hr. On cooling to room temperature the reaction mixture was filtered under suction giving 7.47 g (89%) of a white solid having mp 200° (decomposed to a dark orange liquid). This material was washed with 30 ml of dried ether to remove any benzoic acid. The dried solid had mp 230° dec.

Anal. Calcd for $C_{24}H_{24}O_8Si$: C, 61.52; H, 5.16; Si, 5.99; equiv wt, 117. Found: C, 60.89; H, 5.07; Si, 6.71; equiv wt, 119.

Bis(1,3-diphenyl-1,3-propanediono)diacetato)silicon(IV). In a 50-ml, one-neck, round-bottom flask fitted with a magnetic stirrer and condenser was placed 2.2 g (0.01 mole) of dibenzoylmethane dissolved in 4 ml of dried chloroform. To this was added 1.1 g (0.004 mole) of tetraacetoxysilane dissolved in 1.3 ml of dried chloroform. An intense yellow solution immediately resulted. The solution was then heated to 70–72° for a period of 2 hr. After approximately 0.5 hr at this temperature, a canary yellow precipitate had formed. After cooling, the reaction mixture was filtered under suction. A bright yellow solid (2.0 g, 34%) was collected. It was washed twice with 20-ml portions of petroleum ether, having mp 230–232° dec. The product had a strong odor of acetic acid, was insoluble in boiling chloroform, ethyl acetate, benzene, tetrahydrofuran, and dioxane, and was very soluble in dimethylformamide.

Anal. Calcd for $C_{34}H_{28}O_8Si$: C, 68.90; H, 4.76; Si, 4.74; equiv wt, 148. Found: C, 68.66; H, 4.58; Si, 5.05; equiv wt, 147.

Bis(4,4,4-trifluoro-1-(2-thenyl)-1,3-butanediono)diacetato)silicon(IV). To a slurry containing 2.78 g (0.01 mole) of tetraacetoxysilane in 5 ml of dried chloroform was rapidly added at room temperature 5 g (0.023 mole) of 4,4,4-trifluoro-1-(2-thenyl)-1,3-butanedione. After the initial 15 min, the reaction mixture assumed a milky appearance. On cooling to room temperature the reaction product was removed by filtration under suction and washed with petroleum ether. A light yellow solid (6.0 g, 83%)

was collected which had a strong odor of acetic acid. The material had mp 205° dec.

Anal. Calcd for $C_{20}H_{16}O_8S_2F_6Si$: Si, 4.76; S, 10.85; equiv wt, 147.6. Found: Si, 4.68; S, 10.22; equiv wt, 140.

Transcarboxylation. Monodentate Substitution of Bis(2,4-pentanediono)diacetato)silicon(IV) with Sodium Propionate. In a 100-ml, three-necked, round-bottom flask fitted with a dropping funnel, magnetic stirrer, and thermometer was placed sodium propionate (2.94 g, 0.03 mole) dissolved in 5 ml of dried chloroform. To this was added rapidly a solution containing bis(2,4-pentanediono)diacetato)silicon(IV) (5 g, 0.014 mole) dissolved in chloroform (80 ml). No temperature rise was noted on mixing. The resulting mixture was heated at reflux for 2 hr. After cooling to room temperature the reaction mixture was filtered under suction. The collected solid was then washed with 30 ml of fresh chloroform. After drying it amounted to 2.4 g (54%). To ascertain whether the solid was sodium acetate, the *p*-toluidine derivative was prepared, mp 145° (lit.²² mp 147°).

Anal. Calcd for $C_8H_8O_2Na$: Na, 28.1. Found: Na, 28.1.

The above remaining chloroform filtrate was evaporated under reduced pressure (10 min) at room temperature. The concentrated filtrate was then poured into an excess of petroleum ether. An egg-shell-colored solid, 2.0 g (37%) was collected having mp 145–147°. The melting point of bis(2,4-pentanediono)dipropionato)silicon(IV) prepared by the direct route was 140–150°. A mixture melting point gave no depression.

Anal. Calcd for $C_{16}H_{24}O_8Si$: Si, 7.52. Found: Si, 8.05.

Transcarboxylation. Monodentate Substitution of Bis(2,4-pentanediono)diacetato)silicon(IV) with Sodium Butanate. A similar apparatus to that described above was employed. Bis(2,4-pentanediono)diacetato)silicon(IV) (5.0 g, 0.015 mole) dissolved in 80 ml of chloroform was added rapidly to a suspension containing sodium butanate (3.5 g, 0.03 mole). No increase in temperature was noted on mixing the reagents. After the addition was completed the temperature was raised to 70–72° for 2 hr. A deep orange reaction mixture resulted. After cooling the reaction mixture, it was filtered under suction and washed with 30 ml of fresh chloroform. The chloroform filtrate and washings were combined, and the chloroform solvent was then removed under reduced pressure (50 min) at room temperature. A purple, viscous liquid (3.0 g, 52%) remained which had a strong odor of butyric acid. An infrared spectrum of this material was identical with the spectrum of bis(2,4-pentanediono)di(*n*-butyrate)silicon(IV) prepared by the direct route.

Anal. Calcd for $C_{18}H_{28}O_8Si$: Si, 7.02. Found: Si, 7.95.

Bidentate Exchange. Reaction of Bis(2,4-pentanediono)diacetato)silicon(IV) with Dibenzoylmethane. In a one-neck, 50-ml, round-bottom flask fitted with a magnetic stirrer and condenser was placed a solution containing recrystallized bis(2,4-pentanediono)diacetato)silicon(IV) (0.9 g, 0.0026 mole) in dry chloroform (5.0 ml). To this was added 1.23 g (0.006 mole) of dibenzoylmethane dissolved in 5.0 ml of dry chloroform. The mixture was heated at reflux temperature with stirring for a period of 2 hr. After cooling the resulting mixture to room temperature a yellow solid accumulated. Petroleum ether (5.0 ml) was then added to the reaction mixture. The intense yellow solid (0.62 g, 41%) which formed was collected by filtration under suction, mp 210° dec. An infrared spectrum of this material was similar to that product isolated from the reaction of tetraacetoxysilane and dibenzoylmethane.

Anal. Calcd for $C_{34}H_{28}O_8Si$: Si, 4.74; equiv wt, 148.2. Found: Si, 4.92; equiv wt, 143.0.

Hydrolysis of Bis(1,3-diphenyl-1,3-propanediono)diacetato)silicon(IV). A sample of the above-named compound prepared by the reaction of tetraacetoxysilane with dibenzoylmethane was treated as follows. In a 50-ml, one-neck, round-bottom flask fitted with a magnetic stirrer and condenser was placed 20 ml of approximately 0.5 *N* hydrochloric acid followed by 1.5 g (0.0025 mole) of the chelate derivative. After treating the system at reflux temperature for a period of 24 hr, a milky system resulted. The reaction mixture was then filtered under suction and the collected solid was treated with three 20-ml portions of chloroform. A white, pasty solid remained undissolved after the treatment with chloroform, which was shown to be silicon dioxide. This was indicated by the absence of any charring when it was placed in a Bunsen flame. The chloroform filtrate was concentrated at room temperature under

(22) R. L. Shriner, R. C. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 200.

suction. A yellow crystalline solid, dibenzoylmethane was obtained (1.05 g). This represents 92% recovery of the diketone from the hydrolytic decomposition of the starting material.

A sample of bis(1,3-diphenyl-1,3-propanediono)diacetatosilicon(IV) prepared from the reaction of bis(2,4-pentanediono)diacetatosilicon(IV) and dibenzoylmethane was treated in a similar manner as described above. The chelate (1.2 g, 0.002 mole) gave 0.85 g (93%) of dibenzoylmethane.

Attempted Reaction of Bis(2,4-pentanediono)diacetatosilicon(IV) with Ferric Chloride. In a 125-ml flask was placed 2.5 g (0.007 mole) of bis(2,4-pentanediono)diacetatosilicon(IV) dissolved in 20

ml of dried chloroform. To this was added 1.86 g (0.008 mole) of ferric chloride. A maroon solution formed. The solution was filtered under suction, and the filtrate was poured into 50 ml of dry ether. After cooling in a refrigerator overnight no solid precipitate of iron salt was observed.

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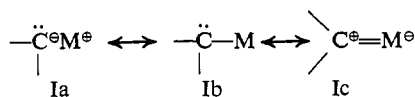
The Synthesis of Aluminols *via* the Addition and Cyclization Reactions of Arylaluminum Compounds¹

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Abstract: In order to study the possible importance of $p_{\pi}-p_{\pi}$ effects in organoaluminum chemistry, a study of the synthesis and properties of vinylaluminum compounds has been undertaken. Aryl-substituted vinylaluminum systems have been prepared by the addition of triphenylaluminum, in turn, to diphenylacetylene, methylphenylacetylene, and 1,3,3,3-tetraphenylpropyne. Examination of the hydrolysis products has permitted considerable insight into the electronic and steric factors involved in such additions. Parallel efforts to add the Al-H bond of diphenylaluminum hydride to alkynes were frustrated by the inability to prepare pure diphenylaluminum hydride from lithium hydride and diphenylaluminum chloride. The foregoing *cis*- β -phenylvinylaluminum compounds were found to undergo a novel metalative cyclization with the formation of the aluminole ring system. The preparation, isolation, and chemical structure proof were carried through in considerable detail for 1,2,3-triphenylbenzaluminole and 5-phenyldibenzaluminole. The mechanistic kinship between the addition of aluminum aryls to alkynes and the metalative formation of aluminols is assessed in terms of reaction conditions and electronic factors. The import of these results to further synthetic and theoretical studies is emphasized.

The importance of carbon-metal bond polarity in correlating the properties of organometallic compounds is abundantly recognized.³ Electron release by a metal center can cause σ bonding to range from almost homopolar linkages (Ib, M = B, Si, Al, etc.) to that of ion pairing (Ia, M = Li, Na, K, etc.). On the other hand, a substantial body of evidence suggests that metals, by virtue of their *np* or *nd* available orbitals, may withdraw electrons from adjacent unsaturated centers by π bonding (Ic). This latter type of



bonding might be especially favored in covalent organometallic compounds where the metal differs little from

carbon in polarity and size. Indeed, physical and chemical evidence has been adduced in support of $p_{\pi}-p_{\pi}$ bonding in vinylboranes⁴ and of $d_{\pi}-p_{\pi}$ bonding in vinylsilanes.⁵ Consequently, the possible significance of such π bonding to an understanding of organoaluminum chemistry has aroused our curiosity and has prompted the study of vinylaluminum compounds. The present report deals with the synthesis and structure proof of certain novel vinylaluminum systems.⁶ Subsequent papers will pursue the nature of the carbon-aluminum bonding as revealed by spectroscopic data.

Of particular interest in this research were aryl-substituted vinylalanes, since the carbon chain conjugation might be expected to enhance the possible importance of carbon-aluminum π bonding (IIa-IIc).

(4) Cf. the appraisal of the properties of vinylboranes by T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(5) (a) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963); (b) R. Summitt, J. J. Eisch, J. T. Trainor, and M. T. Rogers, *J. Phys. Chem.*, **67**, 2362 (1963); (c) L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 1012 (1965); (d) Cf. C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp 91-113.

(6) A preliminary account of the first synthesis of the aluminole system has appeared: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **84**, 1501 (1962).

(1) Part VI of the series, Organometallic Compounds of Group III. Previous paper: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).

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(3) Cf. the lucid treatment of bond polarity by E. G. Rochow, D. T. Hurd, and R. N. Lewis in "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 16-25.