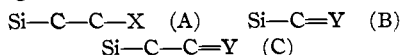


[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

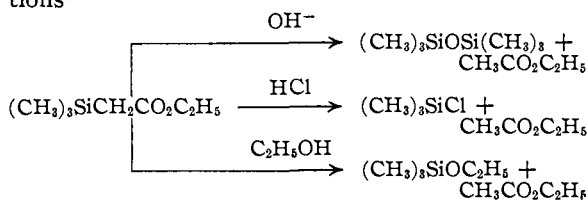
New Silicon-Containing Esters, Acids, Ketones, Alcohols and Halides. Acetoacetic Ester Syntheses with Organosilicon Compounds¹

BY LEO H. SOMMER AND NELSON S. MARANS²

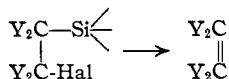
Previous work has shown that the following types of aliphatic groups are in many cases readily cleaved from silicon by electrophilic and nucleophilic reagents



where X is an electronegative group such as halogen or hydroxyl and Y is carbon or oxygen. Ethyl trimethylsilylacetae readily undergoes carbon-silicon cleavage with dilute alkali or acid, hydrogen chloride, and ethanol, according to equations³



In the preparation of trimethylsilylacetic acid, $(\text{CH}_3)_3\text{SiCH}_2\text{CO}_2\text{H}$, precautions must be taken if the bond between the carboxymethyl group and silicon is to remain intact.⁴ The attempted preparation of 3-trimethylsilyl-2-propanone, $(\text{CH}_3)_3\text{SiCH}_2\text{COCH}_3$, from acetyl chloride and trimethylsilylmethylmagnesium chloride gave acetone and hexamethyldisiloxane.^{4a} Although 3-trimethylsilyl-2-propanol, $(\text{CH}_3)_3\text{SiCH}_2\text{CHOHCH}_3$, can be prepared, warming with a small amount of 10% sulfuric acid gives propylene and hexamethyldisiloxane.^{4a} Numerous examples of the β -eliminations of β -haloalkylsilanes which give olefins by 1:2 elimination of silicon and halogen have been reported.⁵



In view of the above data, it appeared that esters, acids, ketones, alcohols, and halides, which conform to structural types A, B or C, would be of limited use, and it therefore seemed desirable to undertake the further synthesis⁶ of compounds

(1) Paper XXVI in a series on organosilicon chemistry: for XXV see *THIS JOURNAL*, **71**, 3254 (1949).

(2) Taken in part from work submitted by N. S. Marans to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

(3) Gold, Sommer and Whitmore, *THIS JOURNAL*, **70**, 2874 (1948).

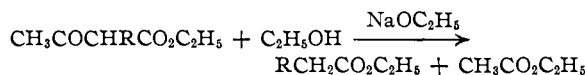
(4) (a) Whitmore, Sommer, Gold and Van Strien, *ibid.*, **69**, 1551 (1947); (b) Sommer, Gold, Goldberg and Marans, *ibid.*, **71**, 1509 (1949).

(5) Cf. Sommer, Bailey and Whitmore, *ibid.*, **70**, 2869 (1948).

(6) The synthesis and some reactions of γ -bromopropyltrimethylsilane, γ -hydroxypropyltrimethylsilane and γ -chloropropyltrichlorosilane, has been reported: Sommer, Van Strien and Whitmore, *THIS JOURNAL*, **71**, 3056 (1949).

in which the functional group is linked to carbon farther removed from silicon, *i.e.*, in the gamma relation to silicon. For this purpose, application of the acetoacetic ester synthesis to haloalkylsilanes proved to be particularly advantageous. Reactions employed in the present work are summarized in Reaction charts I and II.

Reaction of sodioacetoacetic ester with iodomethyltrimethylsilane, $(\text{CH}_3)_3\text{SiCH}_2\text{I}$, has some interesting aspects. Depending upon the relative quantities of sodium and ethyl acetoacetate used, I or IV may be obtained in the largest proportion from this reaction. A 3% excess of sodium gives largely IV, while a slight deficiency of sodium yields mainly I. In the reaction of sodioacetoacetic ester with iodomethylmethylphenylsilane, $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiCH}_2\text{I}$, the only product obtained with a slight excess of acetoacetic ester over sodium was V. These cleavages of the acetyl group from a substituted acetoacetic ester take the form



Reactions of this type which comprise a reversal of the Claisen condensation have been observed previously with purely organic β -ketoesters having one or two substituents on the α -carbon.⁷

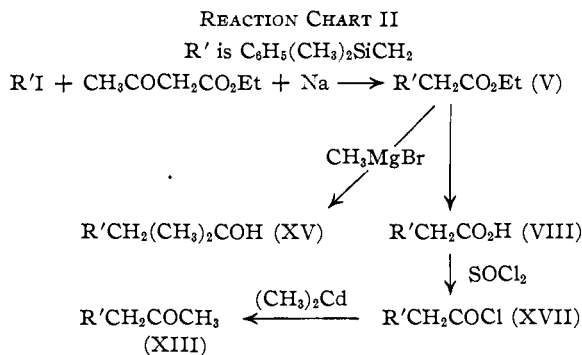
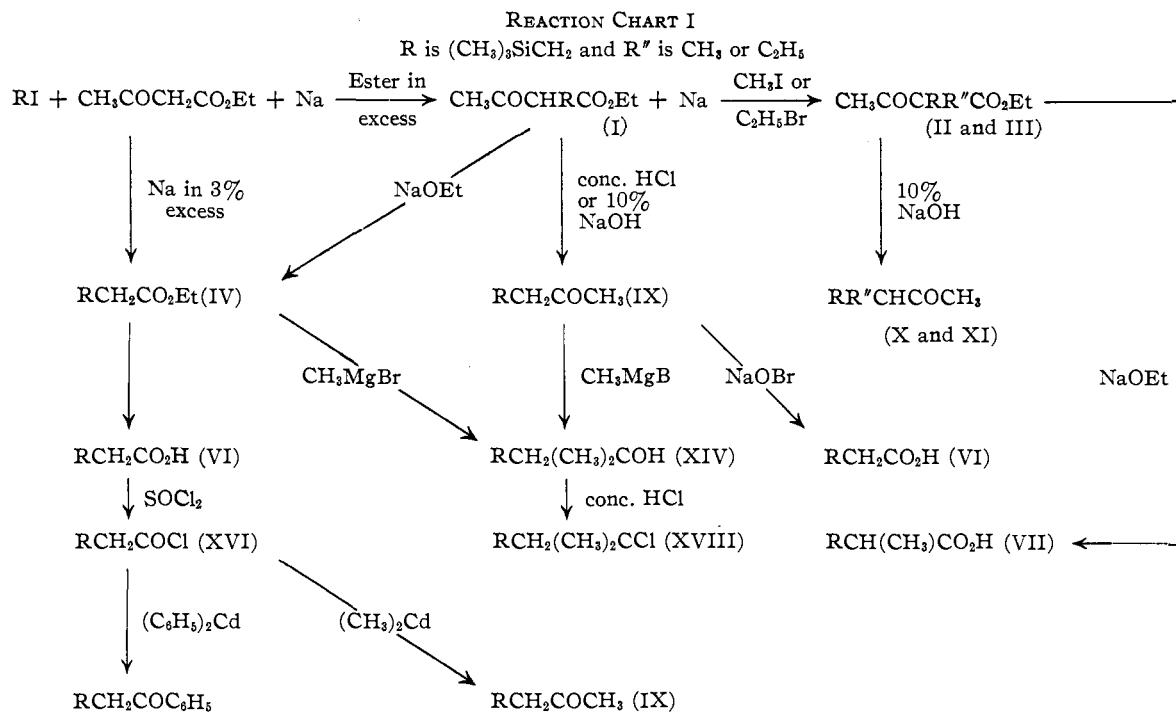
Attempts to prepare II and III from reaction of the sodium derivatives of ethyl α -methylacetoacetate and ethyl α -ethylacetoacetate with iodomethyltrimethylsilane resulted in failure; a similar result was obtained when the sodium derivative of I was treated with iodomethyltrimethylsilane. Thus, introduction of the trimethylsilylmethyl group into a substituted acetoacetic ester has not been achieved. In general, it also appears that iodomethyltrimethylsilane is somewhat less reactive with sodioacetoacetic ester than are ordinary organic halides. For example, *n*-butyl bromide reacts completely with sodioacetoacetic ester during six to ten hours of refluxing of the reaction mixture.⁸ Reaction with iodomethyltrimethylsilane is only 89% complete after thirty hours of reaction at reflux temperature.

The reaction of I and II with sodium ethylate to give the simple esters and their conversion to the acids presented no unusual features. This is in marked contrast to the behavior of ethyl trimethylsilylacetae, which is readily cleaved by acids and bases.

Conversion of I, II and III, to IX, X and XI,

(7) Cf. Beckham and Adkins, *ibid.*, **56**, 1119 (1934).

(8) "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 248.



respectively, was achieved in yields approximating those obtained in such reactions with purely organic β-ketoesters. Formation of these ketones through the use of 10% alkali or concd. hydrochloric acid, and the normal reactions of IX with sodium hypobromite and methylmagnesium bromide, clearly show that *these compounds in which the keto group is linked to carbon gamma to silicon are far more resistant to cleavage of the ketoalkyl group from silicon than are compounds in which the keto group is linked to alpha⁹ or beta carbon.*

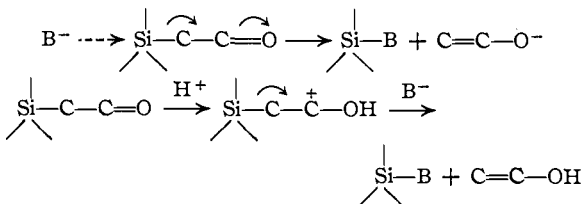
Similar relationships exist between the chemical stabilities of carboxylic acids containing silicon: those in which the carboxy group is linked to alpha carbon undergo cleavage of the carboxyalkyl group from silicon when heated with acid or base for nine hours⁹; the acids here reported, VI, VII and VIII, show no tendency to undergo such cleavages.

Current electronic concepts of the β-elimination

(9) Unpublished work of Sommer and Gold.

and other cleavage reactions of organosilicon compounds having one or more groups conforming to type A, B, or C,⁵ are in harmony with the increased chemical stability which is shown by the compounds herein reported.

For example, in the case of β-ketoalkylsilanes cleavage is made possible by the electron-transfers



However, the ketones, esters and acids here reported are structurally incapable of undergoing carbon-silicon cleavage by the above relatively simple electronic-processes.

Table I lists the eighteen organosilicon compounds prepared in the present work and some of their physical properties. With the exception of VI,^{4b} these compounds have not been reported previously.

Experimental

Ethyl α-Trimethylsilylmethylacetoacetate.—Several reactions of iodomethyltrimethylsilane with sodioacetoacetic ester gave yields of I ranging from 40–60% when a slight excess of acetoacetic ester over sodium was used. The following synthesis is typical.

In a 2-liter, three-necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser, sodium ethylate was prepared by the addition of 30 g., 1.30 moles, of sodium to one liter of absolute ethanol. To this was added, during fifteen minutes, 170 g., 1.31 moles, of ethyl acetoacetate, followed by the addition during thirty minutes

TABLE I

Cmpd.	Name	Formula ^a	B.p.		n_D^{20}	Density d_4^{20}	MR _D	
			°C.	mm.			Calcd. ^d	Found
I	Ethyl α -trimethylsilylmethylacetoacetate	CH ₃ COCHRCO ₂ Et	126	50	1.4405	0.949	59.83	60.1
II	Ethyl α -methyl- α -trimethylsilylmethylacetoacetate	CH ₃ COC(CH ₃)RCO ₂ Et	87	5	1.4420	.9512	64.46	64.04
III	Ethyl α -ethyl- α -trimethylsilylmethylacetoacetate	CH ₃ COC(C ₂ H ₅)RCO ₂ Et	92	3	1.4453	.9509	69.09	68.39
IV	Ethyl β -trimethylsilylpropionate	RCH ₂ CO ₂ Et	93	40	1.4198	.8763	50.51	50.28
V	Ethyl β -phenyldimethylsilylpropionate	R'CH ₂ CO ₂ Et	106	2	1.4972	.9856	70.39	70.13
VI	β -Trimethylsilylpropionic acid	RCH ₂ CO ₂ H ^e	100	6	1.4280	.9196	41.09	40.88
VII	α -Methyl- β -trimethylsilylpropionic acid	RCH(CH ₃)CO ₂ H	92	4	1.4310	.9121	45.72	45.47
VIII	β -Phenyldimethylsilylpropionic acid	R'CH ₂ CO ₂ H	132	2	1.5149	1.037	60.79	60.55
IX	4-Trimethylsilyl-2-butanone	RCH ₂ COCH ₃	84	65	1.4228	0.833	44.17	44.0
X	4-Trimethylsilyl-3-methyl-2-butanone	RCH(CH ₃)COCH ₃	83	40	1.4280	.836	48.80	48.7
XI	3-Trimethylsilylmethyl-2-pentanone	RCH(C ₂ H ₅)COCH ₃	88	30	1.4295	.843	53.43	52.8
XII	3-Trimethylsilyl-1-phenyl-1-propanone	RCH ₂ COC ₆ H ₅	115	4	1.5085	.955	63.99	64.4
XIII	4-Phenyldimethylsilyl-2-butanone	R'CH ₂ COCH ₃	109	4	1.5065	.963	63.99	63.7
XIV	4-Trimethylsilyl-2-methyl-2-butanol ^b	RCH ₂ (CH ₃) ₂ COH	48	4	1.4315	.8255	50.53	50.29
XV	4-Phenyldimethylsilyl-2-methyl-2-butanol ^c	R'CH ₂ (CH ₃) ₂ COH	118	3	1.5058	.9457	70.17	69.78
XVI	β -Trimethylsilylpropionyl chloride	RCH ₂ COCl	92	65	1.4375	.9609	44.95	44.38
XVII	β -Phenyldimethylsilylpropionyl chloride	R'CH ₂ COCl	114	3	1.5188	1.0664	64.50	64.20
XVIII	4-Trimethylsilyl-2-methyl-2-chlorobutane	RCH ₂ (CH ₃) ₂ CCl	90	55	1.4338	0.869	53.64	53.5

^a In the above formulas, R is (CH₃)₃SiCH₂ and R' is C₆H₅(CH₂)₂SiCH₂. ^b Compound XIV has m. p. 12–13°. ^c Compound XV has m. p. 9–10°. ^d Molar refraction was calculated by the bond-refraction method of Warrick, THIS JOURNAL, 68, 2455 (1946). ^e The preparation of compd. VI has been reported, see ref. 4b.

of 300 g., 1.40 moles, of iodomethyltrimethylsilane.¹⁰ The solution was stirred and heated at the reflux point for thirty hours, while determining the extent of reaction by periodic withdrawal of an aliquot which was titrated with standard hydrochloric acid; six hours gave 69% reaction, seventeen hours 85%, twenty-four hours 89%, thirty hours 89%.

From fractionation of the lower-boiling components of the reaction product (b. p. 70–78°), followed by treatment of the distillate with water, and subsequent fractionation of the lower organic layer, there was obtained 67.7 g., 0.31 mole, of iodomethyltrimethylsilane. Iodomethyltrimethylsilane and ethanol form an azeotrope, b. p. 77°, containing about 25% of the former.

The product which remained after fractionation of the lower-boiling material was treated with water, the organic layer was separated, and the aqueous layer extracted with three 300-cc. portions of ether. After drying over anhydrous sodium sulfate, the ether was removed and the product was fractionated in a glass-helix packed column of about ten theoretical plates. There was obtained 113.6 g., 0.523 mole, of I, 48% yield based on unrecovered iodomethyltrimethylsilane.

Anal. Calcd. for C₁₀H₂₀SiO₃: Si, 13.0; mol. wt., 216. Found: Si, 12.9; cryoscopic mol. wt. in benzene, 212.

In addition, there was also obtained 42.9 g., 0.246 mole, of ethyl β -trimethylsilylpropionate (see the following section), 22.6% yield.

Ethyl β -Trimethylsilylpropionate.—Iodomethyltrimethylsilane, 500 g., 2.34 moles, was added with stirring and refluxing during thirty minutes to sodioacetoacetic ester prepared from acetoacetic ester, 296 g., 2.28 moles, and sodium ethylate, 2.35 moles, in one liter of ethanol. The reaction mixture was heated at the reflux point for fourteen hours while following the reaction by titration of aliquots with standard acid: two hours gave 50% reaction; twelve hours, 90%; and fourteen hours, 91%. After cooling, the reaction product was neutralized with 15 cc. of glacial acetic acid.

Fractionation of the lower-boiling material (70–78°) gave an ethyl acetate-ethanol azeotrope which represented a 64% yield of ethyl acetate based on the starting aceto-

acetic ester (after correcting for ethyl acetate from the added acetic acid), and iodomethyltrimethylsilane-ethanol azeotrope from which there was recovered 64 g., 0.3 mole, of iodomethyltrimethylsilane.

The product remaining from the above fractionation was treated with water, the organic layer was separated, and the aqueous layer was extracted with three 200-cc. portions of ether. After drying over anhydrous sodium sulfate fractionation gave 250 g., 1.43 moles, of ethyl β -trimethylsilylpropionate, 70% yield.

Anal. Calcd. for C₈H₁₈SiO₃: Si, 16.1; sapn. equiv., 174. Found: Si, 16.2; sapn. equiv., 172.

Ethyl β -trimethylsilylpropionate was also prepared from the reaction of one mole of sodium ethylate in 300 cc. of ethanol with 30 g., 0.139 mole, of compound I. The reactants were heated at 90° for twelve hours, and then 60 g., 1.0 mole, of acetic acid was added to neutralize the sodium ethylate. The sodium acetate which precipitated was dissolved by the addition of 75 cc. of water, the ethanol was carefully fractionated, and the fractions collected as steam distillate were combined with the residual material. After treatment with water, the organic layer was separated and the aqueous layer extracted with three 200-cc. portions of ether. Fractionation gave compound IV in 64% yield.

Ethyl α -Methyl- α -trimethylsilylmethylacetoacetate.—Compound I, 50 g., 0.22 mole, was added to a solution of 0.22 mole of sodium ethylate in 300 cc. of ethanol during fifteen minutes. Addition of methyl iodide, 40 g., 0.280 mole, with stirring was followed by refluxing of the reaction mixture for thirty minutes. The major part of the ethanol was then removed by distillation, and the remaining product was then treated with water. The organic layer was separated and the aqueous layer extracted with three 100-cc. portions of ether. After drying over anhydrous sodium sulfate, fractionation gave 38.3 g., 0.160 mole, of compound II, 72.4% yield.

Anal. Calcd. for C₁₁H₂₂SiO₃: Si, 12.2; mol. wt., 230. Found: Si, 12.0; mol. wt. in benzene, 224.

Ethyl α -Ethyl- α -trimethylsilylmethylacetoacetate.—Ethyl α -trimethylsilylmethylacetoacetate, 0.231 mole, was converted to the sodium derivative and treated with 0.360 mole of ethyl bromide by a procedure closely similar to that

(10) Whitmore and Sommer, THIS JOURNAL, 66, 481 (1946).

used for the synthesis of compound II. The desired product was obtained in 58% yield.

Anal. Calcd. for $C_{12}H_{24}SiO_3$: Si, 11.5; mol. wt., 224. Found: Si, 11.6; mol. wt. in benzene, 239.

Ethyl β -Phenyldimethylsilylpropionate.—Ethyl acetate, 128 g., 0.984 mole, was added to a stirred solution of 0.978 mole of sodium ethylate in 700 cc. of ethanol during fifteen minutes. During an additional thirty minutes, there was added 281 g., 1.02 moles, of iodomethyldimethylphenylsilane.¹¹ After heating the reaction mixture to reflux, titration of aliquot portions of the reaction mixture for completeness of reaction gave the following data: 54% reaction after four hours; 62%, fifteen hours; 75%, nineteen hours; 80%, twenty-three hours; 93%, forty hours. Fractionation gave 109.6 g., 0.464 mole, of compound V, a yield of 47%. Iodomethyldimethylphenylsilane was recovered in 30% yield. Thus, the yield of V based on unrecovered halide was 67%.

Anal. Calcd. for $C_{15}H_{26}SiO_2$: Si, 11.9; sapon. equiv., 236. Found: Si, 11.8; sapon. equiv., 235.

β -Trimethylsilylpropionic Acid.—A mixture of 264 g., 1.51 moles, of ethyl β -trimethylsilylpropionate with 1000 cc. of 10% sodium hydroxide solution was stirred and heated at 90° for two hours in a 2-liter, three-necked flask equipped with a stirrer and a reflux condenser. After cooling, the solution was acidified with concd. hydrochloric acid and the upper layer was separated. After drying over sodium sulfate, fractionation gave 197 g., 1.35 moles, of VI, 89% yield.

Anal. Calcd. for $C_8H_{14}SiO_2$: Si, 19.2; neut. equiv., 146. Found: Si, 19.1; neut. equiv., 145.

α -Methyl- β -trimethylsilylpropionic Acid.—Compound II, 52 g., 0.23 mole, was added to a solution of 0.861 mole of sodium ethylate in 400 cc. of ethanol and the reaction mixture was stirred and heated at 90° for twelve hours. The low-boiling material was removed by distillation and the residue was treated with water and then acidified with concentrated hydrochloric acid. The organic layer was separated and the aqueous layer extracted with three 100-cc. portions of ether. After drying over sodium sulfate, fractionation gave 24.1 g., 0.151 mole, of VII, 67% yield.

Anal. Calcd. for $C_7H_{13}SiO_2$: Si, 17.5; neut. equiv., 160. Found: Si, 17.4; neut. equiv., 159.

β -Phenyldimethylsilylpropionic Acid.—A mixture of 150 cc. of 10% sodium hydroxide solution and 40 g., 0.17 mole, of compound V was stirred and heated at 80° for two hours. After cooling in an ice-bath, concentrated hydrochloric acid was added dropwise with stirring until the mixture was slightly acid. (The careful acidification is to prevent hydrolytic cleavage of the phenyl group from silicon.) The organic layer was separated and the aqueous layer was made more strongly acid. The aqueous layer was then extracted with two 100-cc. portions of ether and the combined organic layers were dried over sodium sulfate. Fractionation gave 29.1 g., 0.141 mole, of VIII, 82.4% yield.

Anal. Calcd. for $C_{11}H_{18}SiO_2$: Si, 13.5; neut. equiv., 208. Found: Si, 13.5; neut. equiv., 207.

4-Trimethylsilyl-2-butanone.—In a 500-cc. three-necked flask equipped with a stirrer and a reflux condenser there were placed 24.0 g., 0.111 mole, of ethyl α -trimethylsilylmethylacetate, 80 cc. of concd. hydrochloric acid, and 80 cc. of ethanol. The reaction mixture was stirred and heated at 90° until no observable organic layer was present (four hours). Addition of ether and saturation of the solution with sodium chloride gave an organic layer which was separated. After extraction of the aqueous layer with three 200-cc. portions of ether, the combined organic layers were dried over sodium sulfate. Fractionation gave 9.5 g., 0.065 mole, of compound IX, 59% yield.

(11) Prepared from the corresponding chloride by reaction with sodium iodide in acetone. Synthesis of these compounds will be described in a forthcoming publication.

Anal. Calcd. for $C_7H_{11}SiO$: Si, 19.5; mol. wt., 144. Found: Si, 19.6; mol. wt. in benzene, 146.

4-Trimethylsilyl-2-butanone was also prepared in better yield by the following procedure. A mixture of 81 g., 0.370 mole, of I, and 400 cc. of 10% sodium hydroxide was stirred and heated at 90° for twelve hours. The organic layer was separated, the aqueous layer extracted with ether, and the combined organic material was dried over sodium sulfate. Fractionation gave 43.0 g., 0.3 mole, of compound IX, 81% yield.

4-Trimethylsilyl-3-methyl-2-butanone.—Using a procedure similar to that employed for IX, a 53% yield of X was obtained by heating II with 10% sodium hydroxide.

Anal. Calcd. for $C_9H_{15}SiO$: Si, 17.7; mol. wt., 158. Found: Si, 17.8; mol. wt. in benzene, 160.

3-Trimethylsilylmethyl-2-pentanone.—By a procedure similar to that used for compounds IX and X, compound XI was obtained from III by ketonic cleavage with 10% sodium hydroxide solution in 20% yield. Compound III was recovered to the extent of 40%.

Anal. Calcd. for $C_8H_{16}SiO$: Si, 16.3. Found: Si, 16.3.

β -Trimethylsilylpropionyl Chloride and 3-Trimethylsilyl-1-phenyl-1-propanone.— β -Trimethylsilylpropionic acid, 40 g., 0.274 mole, was heated with 50.4 g., 0.424 mole, of thionyl chloride for one hour at 90°. Fractionation gave 40.3 g., 0.245 mole, of β -trimethylsilylpropionyl chloride, 89% yield.

Anal. Calcd. for $C_8H_{13}SiOCl$: Si, 17.0; neut. equiv., 82.3. Found: Si, 16.7; neut. equiv., 82.2.

Phenylmagnesium bromide was prepared in the usual manner from 7.5 g., 0.31 mole, of magnesium, 300 cc. of ether, and 70 g., 0.45 mole, of bromobenzene. The solution was then cooled to 0° and 30 g., 0.16 mole, of cadmium chloride was added during five minutes. After removal of the major portion of the ether by distillation, 300 cc. of benzene was added and an additional portion of ether was removed by heating on the steam-bath. While heating the reaction flask on the steam-bath, there was added 21.5 g., 0.131 mole, of β -trimethylsilylpropionyl chloride in five minutes. After heating for an additional twenty minutes, the reaction product was poured into a mixture of hydrochloric acid and ice. The organic layer was then separated, the aqueous layer extracted with two 100-cc. portions of benzene, and the combined organic layers washed with water, 5% carbonate solution, and water. After drying over sodium sulfate, fractionation gave 10 g., 0.048 mole, of compound XII, 37% yield.

Anal. Calcd. for $C_{12}H_{19}SiO$: Si, 13.6; mol. wt., 206. Found: Si, 13.5; mol. wt., 210.

Reaction of dimethylcadmium with β -trimethylsilylpropionyl chloride was performed as an added structure proof for compound IX. Dimethylcadmium was prepared from methylmagnesium bromide, 0.31 equivalent, and treated with β -trimethylsilylpropionyl chloride, 0.151 mole, by essentially the same procedure used for synthesis of compound XII. There was obtained 10.7 g., 0.074 mole, of 4-trimethylsilyl-2-butanone, b. p. 80° at 50 mm., n_D^{20} 1.4230, 50% yield.

β -Phenyldimethylsilylpropionyl Chloride and 4-Phenyldimethylsilyl-2-butanone.— β -Phenyldimethylsilylpropionic acid, 24 g., 0.115 mole, was heated with 58 g., 0.49 mole, of thionyl chloride at 90° for two hours. Fractionation gave 15.9 g., 0.0702 mole, of compound XVII, 61% yield.

Anal. Calcd. for $C_{11}H_{15}SiOCl$: Si, 12.4; neut. equiv., 113. Found: Si, 12.4; neut. equiv., 112.

β -Phenyldimethylsilylpropionyl chloride, 12.5 g., 0.055 mole, was treated with dimethylcadmium by a procedure similar to that used with XVI. After the mixture had been stirred and heated for one hour at 80°, it was cooled and poured into ice-water. The emulsion that formed was broken by acidification of the mixture with acetic acid. The organic layer was separated and the aqueous layer extracted with two 100-cc. portions of benzene. The combined organic materials were washed with aqueous potas-

sium carbonate, with water, and then the benzene was removed by distillation. Fractionation gave 5.2 g., 0.0253 mole, of XIII, 45% yield.

Anal. Calcd. for $C_{12}H_{18}SiO$: Si, 13.6; mol. wt., 206. Found: Si, 13.6; mol. wt., 202.

4-Trimethylsilyl-2-methyl-2-butanol.—To a rapidly stirred solution of methylmagnesium bromide, 0.51 equivalent, in 500 cc. of ether, there was added 30 g., 0.172 mole, of ethyl β -trimethylsilylpropionate over a period of fifteen minutes while cooling the reaction flask in an ice-bath. The cold reaction mixture was hydrolyzed with ice and water and the organic layer was separated. The aqueous layer was made slightly acid with hydrochloric acid and was extracted with two 100-cc. portions of ether. The combined organic layers were washed with 10% carbonate solution and dried over anhydrous sodium sulfate. Fractionation gave 17.3 g., 0.108 mole, of compound XIV, a yield of 63%.

Anal. Calcd. for $C_8H_{20}SiO$: Si, 17.5; mol. wt., 162. Found: Si, 17.7; mol. wt. in benzene, 165.

Compound XIV was also prepared from 4-trimethylsilyl-2-butanone. To a solution of methylmagnesium bromide, 0.41 mole, in 400 cc. of ether, there was added with stirring 33 g., 0.229 mole, of 4-trimethylsilyl-2-butanone during one hour. After refluxing had ceased, the reaction mixture was heated for an additional hour, hydrolyzed with ice and water, and the organic layer was separated. The aqueous layer was made slightly acid with hydrochloric acid and was then extracted with two 100-cc. portions of ether. The combined organic layers were washed with 5% carbonate solution and dried over sodium sulfate. After removal of the ether, fractionation gave 30.1 g., 0.188 mole, of 4-trimethylsilyl-2-methyl-2-butanol which had physical properties which checked those obtained on the material prepared from compound IV. The yield was 82%.

4-Phenyldimethylsilyl-2-methyl-2-butanol.—To a solution of methylmagnesium bromide, 0.43 mole, in 500 cc. of dry ether, there was rapidly added 25.5 g., 0.108 mole, of ethyl β -phenyldimethylsilylpropionate while cooling the reaction flask in an ice-bath. After stirring and refluxing for one hour, the product was poured into a mixture of ice and water, and the organic layer was separated. The aqueous layer was treated with hydrochloric acid until slightly acidic, and was then extracted with two 100-cc. portions of ether. The combined organic layers were washed with 5% sodium bicarbonate solution, with water,

and were then dried over sodium sulfate. Fractionation gave 19.2 g., 0.0865 mole, of compound XV, 80% yield.

Anal. Calcd. for $C_{13}H_{22}SiO$: Si, 12.7; mol. wt., 222. Found: Si, 12.9; mol. wt. in benzene, 221.

4-Trimethylsilyl-2-methyl-2-chlorobutane.—Compound XIV, 6.7 g., 0.042 mole, was shaken with 100 cc. of concd. hydrochloric acid in a separatory funnel for fifteen minutes. The organic layer was then separated, washed with 5% bicarbonate solution followed by water, and was then dried over calcium chloride. Fractionation gave 3.6 g., 0.020 mole, of XVIII, 48% yield.

Anal. Calcd. for $C_8H_{18}SiCl$: Si, 15.7; Cl, 19.9. Found: Si, 15.8; Cl, 19.9.

Reaction of 4-Trimethylsilyl-2-butanone with Sodium Hypobromite.—In a 2-liter, three-necked flask equipped with a stirrer, dropping funnel, and a condenser, and surrounded by an ice-salt-bath, there was placed a solution of 57.2 g., 1.43 moles, of sodium hydroxide in 500 cc. of water. Bromine, 82.8 g., 0.52 mole, was then added at such a rate that the temperature remained below 0°. To this solution, over a period of one hour, while maintaining the temperature at 5°, there was added 25.0 g., 0.173 mole, of 4-trimethylsilyl-2-butanone. The reaction mixture was stirred at 0° for one hour and then for three hours at 25°. The lower organic layer was separated and the aqueous layer extracted with three 100-cc. portions of ether. The aqueous layer was then acidified with 75 cc. of concd. hydrochloric acid, the organic layer separated, and the aqueous layer extracted with three 100-cc. portions of ether. The combined organic layers from the acidified aqueous layer were dried over sodium sulfate and fractionated. There was obtained 10.3 g., 0.071 mole, of compound VI, b. p. 122° at 30 mm., n_D^{20} 1.4280, 41% yield.

Summary

1. The acetoacetic ester synthesis has been successfully applied to iodomethylsilanes.
2. Seventeen new silicon-containing esters, acids, ketones, alcohols, and halides, have been synthesized. In these compounds the functional group is linked to a carbon atom in the gamma relation to silicon: $Si-C-C-C-X$ and $Si-C-C-C=O$, where X is halogen or hydroxyl.

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Partition Studies on Phenols. IV. Isolation of Indanols from Coal Hydrogenation Oils¹

By C. GOLUMBIC, E. O. WOOLFOLK, R. A. FRIEDEL AND M. ORCHIN

The hydrogenation of coal produces, among other products, a complex mixture of phenolic compounds. Because of their potential commercial value and the importance of oxygenated compounds in the study of the mechanism of the liquefaction of coal,² considerable effort has been devoted to the characterization of the phenolic fraction of coal hydrogenation oil. As a result, sixteen individual phenols have been isolated or identified,

and the quantity of each in a particular mixture has been estimated or accurately determined.³

Of the many tools and techniques successfully employed in this work, the countercurrent distribution technique of Craig^{4,5} was particularly useful, especially in the high-boiling range. Our pre-

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(2) H. H. Storch, C. H. Fisher, C. O. Hawk and A. Eisner, *Bur. Mines Tech. Paper 654*, 50 pp. (1943).