plastic, non-elastic, fully saturated product was obtained. No method was found for purification of the product.

Anal. Calcd. for $C_{13}H_{22}O_4Sn$: C, 43.25; H, 6.1; Sn, 32.91; neut. equiv., 180.4. Found: C, 40.33; H, 5.41; Sn, 28.59; neut. equiv., 188.

Dibutyltin 3-Methyladipate.—Molecular proportions of dibutyltin diacetate (5.03 g.) and 3-methyladipic acid (11.02 g.) were allowed to react at a gradual temperature rise in 300 ml. of xylene with azeotropic distillation until the by-product acetic acid was removed (91%). The xylene was then mostly removed by distillation and replaced by a 50/50 mixture of benzene and petroleum ether and warmed. The solution was cooled to −10° and left two days to crystallize. It was then filtered and washed with cold petroleum ether. The yield was 80% of crystalline material of m.p. 143–144.5°. The yield of product was 9.5 g. (78%).

Anal. Calcd. for $C_{15}H_{28}O_4Sn$: C, 46.07; H, 7.17; Sn, 30.08; neut. equiv., 195.4; mol. wt., 390.7. Found: C, 45.80; H, 7.30; Sn, 29.66; neut. equiv., 205; mol. wt., 800 (f.p. in benzene), 783 (Rast in camphor).

NATICK, MASSACHUSETTS

[CONTRIBUTED FROM THE RESEARCH LABORATORIES OF THE DOW CORNING CORPORATION]

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part III. The Addition to Non-terminal Olefins in the Presence of Chloroplatinic Acid

BY JOHN C. SAAM AND JOHN L. SPEIER

RECEIVED FEBRUARY 5, 1958

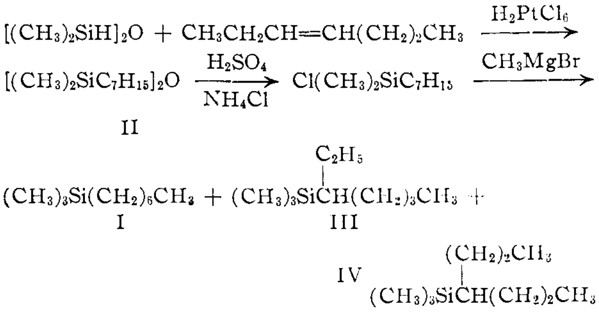
In the presence of chloroplatinic acid, trichlorosilane methyldichlorosilane or dimethylchlorosilane and heptene-3 formed *n*-heptylchlorosilanes in good yields. Symmetrical tetramethyldisiloxane and heptene-3 formed 1,3-di-*n*-heptyltetramethyldisiloxane along with smaller amounts of the 3- and 4-heptyl isomers.

The unexpected formation of *n*-pentylsilanes from pentene-2 and methyldichlorosilane or trichlorosilane in the presence of chloroplatinic acid, ruthenium chloride or platinum-on-charcoal has recently been described.[1] The novelty of this result prompted an investigation of the addition of various silicon hydrides to heptene-3 where the terminal position of the olefin is more remote from the double bond and is less subject to inductive or resonance effects.

Refluxing trichlorosilane with heptene-3 in the presence of chloroplatinic acid resulted in excellent yields of *n*-heptyltrichlorosilane. The product was converted with excess methylmagnesium bromide to the known heptyltrimethylsilane (I)[2] and compared with an authentic sample prepared from trimethylchlorosilane, *n*-heptyl chloride and sodium.[3] A gas–liquid phase chromatogram and an infrared spectrum of the trimethyl derivative of the adduct revealed that it was free of isomers and identical with the authentic sample. Likewise, methyldichlorosilane and dimethylchlorosilane reacted with heptene-3 in the presence of chloroplatinic acid to form only the *n*-heptylsilanes in good yields, and in each case the products were converted to *n*-heptyltrimethylsilane (I) which was identical with the authentic sample and free of isomers.

One siloxane, *sym*-tetramethyldisiloxane, was found to yield a mixture of 1,3-diheptyltetramethyldisiloxane, (II). The mixture was converted to the heptyltrimethylsilanes by employing the flood reaction.[4]

A gas-liquid phase chromatogram of the heptyltrimethylsilanes revealed three components, the major component being identical with *n*-heptyltrimethylsilane (I). The two minor components were identical to the authentic mixed 3- and 4-heptyltrimethylsilanes which were prepared by the addition of trichlorosilane to heptene-3 in the presence of acetyl peroxide[5] followed by treatment of the adduct with excess methylmagnesium bromide. The results of the addition of various silicon hydrides to heptene-3 are summarized in the table.



$$[(CH_3)_2SiH]_2O + CH_3CH_2CH{=}CH(CH_2)_2CH_3 \xrightarrow{H_2PtCl_6} \underset{\text{II}}{[(CH_3)_2SiC_7H_{15}]_2O} \xrightarrow[NH_4Cl]{H_2SO_4} Cl(CH_3)_2SiC_7H_{15} \xrightarrow{CH_3MgBr}$$

$$\underset{\text{I}}{(CH_3)_3Si(CH_2)_6CH_3} + \underset{\text{III}}{(CH_3)_3Si\overset{\overset{C_2H_5}{|}}{C}H(CH_2)_3CH_3} + \underset{\text{IV}}{(CH_3)_3Si\overset{\overset{(CH_2)_2CH_3}{|}}{C}H(CH_2)_2CH_3}$$

These results and others[1] indicated a strong tendency for the chlorosilyl group of the silicon hydride to add to the terminal position of the olefin, even when the double bond was as remote as two carbon atoms from the terminal position. This tendency appeared to have been somewhat weakened when the silicon hydride was a siloxane.

A plausible explanation of these results could require a nucleophilic attack at the double bond by a hydride ion, brought about by the catalyst. The resulting 3- or 4-secondary carbanion (A) would tend to acquire a more stable configuration by transmitting the negative charge to the terminal position through the transition states B or B′. Transition state B is a series or a cascade of "α-hydrogen bonds"[6] involving the protons along the chain; whereas transition state B′ is a five- or six-membered cyclic in which a terminal proton is

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[1] J. L. Speier, J. A. Webster and G. H. Barnes, THIS JOURNAL, **79**, 974 (1957).

[2] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. VanStrien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, *ibid.*, **68**, 475 (1946), report b.p. 184° at 760 mm., $n^{20}D$ 1.4201, d^{20}_4 0.7506.

[3] J. L. Speier, *ibid.*, **74**, 1003 (1952).

[4] E. A. Flood, *ibid.*, **55**, 1735 (1933).

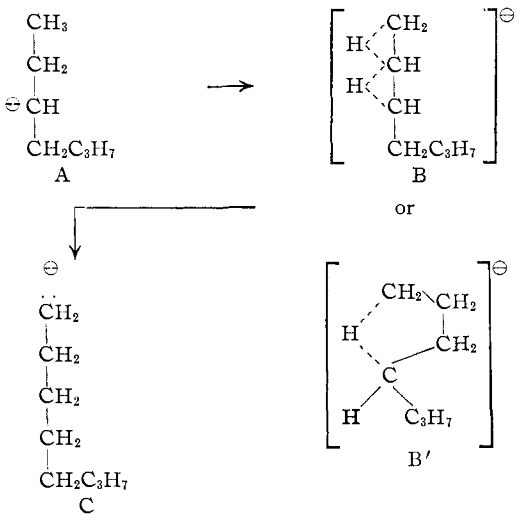
[5] J. L. Speier, R. Zimmerman and J. Webster, *ibid.*, **78**, 2278 (1956); L. H. Sommer, E. Pietruza and F. C. Whitmore, *ibid.*, **69**, 188 (1947).

[6] M. M. Kreevoy and H. Eyring, *ibid.*, **79**, 5121 (1957).

Adducts of heptene-3		$(CH_3)_3SiC_7H_5$ derivative[a,b]			
Silicon hydride	Product	Yield, %	B.p., °C., (750 mm.)	n^{25}_D	d^{25}_4
Cl_3SiH	n-$C_7H_{15}SiCl_3$	91.6	183.5	1.4184	0.7464
CH_3HSiCl_2	n-$C_7H_{15}SiCH_3Cl_2$	93.1	184.0	1.4185	.7465
$(CH_3)_2HSiCl$	n-$C_7H_{15}Si(CH_3)_2Cl$	60.8	183.5	1.4184	.7465
$[(CH_3)_2SiH]_2O$	$[C_7H_{15}(CH_3)_2Si]_2O$	87.5	180–183	1.4222–1.4170	0.7566–0.7491

[a] Authentic n-heptyltrimethylsilane has b.p. 184° at 750 mm., n^{25}_D 1.4186, d^{25}_4 0.7466. [b] An authentic mixture of 3- and 4-heptyltrimethylsilane has b.p. 173.5–176° at 750 mm. n^{25}_D 1.4262, d^{25}_4 0.7622–0.7620.

bridged to the 3- or 4- carbon atom. The net result would be a primary carbanion which would lead to the observed products after a nucleophilic attack on a silicon atom



This mechanism can be supported by the following observations: 1. Neither 2- nor 3-olefins rearrange under these experimental conditions. It was not possible to isolate anything but heptene-3 from the reaction mixtures when it was present in excess. Also, the 2-heptyl isomer was absent from the reaction mixtures of heptene-3 and the chlorosilanes or *sym*-tetramethyldisiloxane. 2. There is no reason to suspect that the n-heptylchlorosilanes resulted from the rearrangement of the 3- or 4-heptyl isomer since it has been demonstrated that the analogous 2- and 3-alkylchlorosilanes were stable under these experimental conditions.[1] 3. An aliphatic carbonium ion or free radical, where the positive charge or electron is stabilized at a secondary position by inductive or conjugative effects,[7] is not a probable intermediate. However, Pines and Mark[8] observed that the relative order of decreasing stability of aliphatic carbanions is primary > secondary > tertiary.

The fact that *sym*-tetramethyldisiloxane gave a mixture of the 1-, 3- and 4-heptyl isomers with heptene-3 suggested that the nucleophilic attack on silicon by A was at a rate comparable to that at which A rearranged to the primary carbanion C.

Experimental

The heptene-3 was obtained from the Special Products Division of the Phillips Petroleum Co., Bartlesville, Okla., and revealed only one component on a gas liquid phase chromatogram. The heptyl chloride was the Eastman Kodak Co. White Label grade.

***n*-Heptyltrichlorosilane.**—A mixture of 147 g. (1.5 moles) of heptene-3, 203 g. (1.5 moles) of trichlorosilane and 0.5 ml. of 0.1 molar alcoholic chloroplatinic acid (5×10^{-5} mole) was refluxed for 24 hours. During this period the temperature of the refluxing mixture increased from 55 to 190°. The mixture was distilled through a 22 mm. × 4 ft. Podbielniak column packed with Heli-pak to give 320 g. (91.6% yield) of pure n-heptyltrichlorosilane, b.p. 211° at 740 mm., n^{25}_D 1.4439, d^{25}_4 1.087; R_D found 0.244, R_D calcd. 0.244.

Anal. Calcd. for $SiC_7H_{15}Cl_3$: neut. equiv., 77.8; Si, 12.04. Found: neut. equiv., 77.7; Si, 12.00.

A similar run was carried out using 98 g. (1 mole) of heptene-3 and 101.6 g. (0.75 mole) of trichlorosilane. The mixture was distilled before the reaction had gone to completion to give 129 g. (74% conversion, 100% yield based on unrecovered heptene-3) of n-heptyltrichlorosilane and 42.5 g. of heptene-3 free of other isomers.

***n*-Heptyltrimethylsilane.**—To four moles of methylmagnesium bromide in 1.5 l. of ether was added slowly 233.5 g. (1 mole) of the n-heptyltrichlorosilane. After the addition was complete, the mixture was refluxed one hour and two-thirds of the ether was removed by distillation. Then a saturated solution of 210 g. of ammonium chloride was added to the stirred mixture; the organic layer was separated and was distilled through a 22 mm. × 120 cm. Podbielniak column packed with Heli-pak. This resulted in 139 g. (80.6% yield) of n-heptyltrimethylsilane, b.p. 183.5° at 740 mm., n^{24}_D 1.4184, d^{25}_4 0.7464; found R_D 0.338, calcd. R_D 0.338. A gas–liquid phase chromatogram of the product indicated only one component, and it was indistinguishable from authentic n-heptyltrimethylsilane. The infrared spectra of the product and authentic n-heptyltrimethylsilane were also indistinguishable.

***n*-Heptylmethyldichlorosilane.**—To 98 g. (1 mole) of heptene-3 containing 0.5 ml. of a 0.1 molar solution of chloroplatinic acid (5×10^{-5} mole) previously heated to 70° was added slowly 115 g. (1 mole) of methyldichlorosilane. The chlorosilane was added at a rate that would maintain a temperature of 120° in the reacting mixture. After the addition was complete, the product, isolated in a manner similar to that of the n-heptyltrichlorosilane, was obtained in a 93.1% yield (198 g.) b.p. 207.5° at 750 mm., n^{25}_D 1.4396, d^{25}_4 0.9780; found R_D 0.269, calcd. R_D 0.269.

Anal. Calcd. for $SiC_8H_{18}Cl_2$: neut. equiv., 106.6; Si, 13.15. Found: neut. equiv., 107.8; Si, 13.55.

The n-heptylmethyldichlorosilane was converted with excess methylmagnesium bromide in the previously described manner to n-heptyltrimethylsilane in 93% yields, b.p. 184° at 750 mm., n^{25}_D 1.4185, d^{25}_4 0.7465; found R_D 0.338, calcd. R_D 0.338. A gas–liquid phase chromatogram of this product indicated that only one component was present, and it was indistinguishable from authentic n-heptyltrimethylsilane. The infrared spectra of this product and authentic n-heptyltrimethylsilane were also indistinguishable.

***n*-Heptyldimethylchlorosilane.**—A mixture of 185.8 g. (1.89 moles) of heptene-3, 202.5 g. (2.14 moles) of a crude grade of dimethylchlorosilane (contaminated with about 30% of lower boiling hydrocarbons) and 0.5 ml. of a 0.1 molar alcoholic solution of chloroplatinic acid (5×10^{-5} mole) was refluxed for 72 hours. The product was isolated in the usual manner to give 221 g. (60.8% yield) of pure n-heptyldimethylchlorosilane, b.p. 204° at 745 mm., n^{25}_D 1.4311, d^{25}_4 0.8639; found R_D 0.299, calcd. R_D 0.299. The only other components of the mixture were heptene-3 and dimethylchlorosilane.

Anal. Calcd. for $SiC_9H_{21}Cl$: neut. equiv., 192.5. Found: neut. equiv., 192.9.

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[7] For examples and discussion of the stabilization of free radicals and carbonium ions, see reference 6; A. Kossiakoff and F. O. Rice, THIS JOURNAL, **65**, 590 (1943); and E. R. Alexander, "Principles of Organic Ionic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 41.

[8] H. Pines and V. Mark, THIS JOURNAL, **78**, 4316 (1956); **78**, 5946 (1956).

The *n*-heptyldimethylchlorosilane was converted by the previously described manner to *n*-heptyltrimethylsilane in a 77.6% yield, b.p. 183.5° at 750 mm., $n^{25}{}_D$ 1.4184, $d^{25}{}_4$ 0.7465; found *R*D 0.338, calcd. *R*D 0.338.

A gas-liquid phase chromatogram of the *n*-heptyltrimethylsilane indicated only one component, and it was indistinguishable from authentic *n*-heptyltrimethylsilane. The infrared spectra of this product and authentic *n*-heptyltrimethylsilane were also indistinguishable.

1,3-Di-*n*-heptyltetramethyldisiloxane from *n*-Heptyldimethylchlorosilane.—One hundred grams (0.52 mole) of the *n*-heptyldimethylchlorosilane in 100 ml. of ether was poured over crushed ice. The organic layer was separated, washed neutral, and the solvent was removed in a vacuum. The product was distilled at reduced pressure to give 75 g. (87.5% yield) of 1,3-di-*n*-heptyltetramethyldisiloxane, b.p. 178–180° at 20 mm., $n^{25}{}_D$ 1.4305, $d^{25}{}_4$ 0.8170; found *R*D 0.316, calcd. *R*D 0.316.

Anal. Calcd. for $Si_2C_{18}H_{42}O$: Si, 17.51. Found: Si, 17.46.

1,3-Di-*n*-heptyltetramethyldisiloxane from Heptene-3 and *sym*-Tetramethyldisiloxane.—A mixture of 157 g. (1.6 moles) of heptene-3, 100.5 g. (0.75 mole) of *sym*-tetramethyldisiloxane and 0.75 ml. of a 0.1 molar alcoholic solution of chloroplatinic acid (7.5 × 10^{-5} mole) was refluxed for 48 hours. The mixture was distilled to give 216 g. (87.5% yield) of 1,3-diheptyltetramethyldisiloxane, b.p. 162–190° at 18 mm., $n^{25}{}_D$ 1.4308–1.4302, $d^{25}{}_4$ 0.8274–0.8246; found *R*D 0.316, calcd. *R*D 0.316.

Anal. Calcd. for $Si_2C_{18}H_{42}O$: Si, 17.51. Found: Si, 17.37.

To a dispersion of 218 g. (0.66 mole) of the 1,3-diheptyltetramethyldisiloxane in 400 ml. of concd. sulfuric acid was added 100 g. of ammonium chloride. Then dry hydrogen chloride was passed through the stirred dispersion for 2 hours. The layers were allowed to separate, and a 96.5-g. portion (0.5 mole) of the upper layer (crude heptyldimethylchlorosilane) was added slowly with stirring to a solution of 1 mole of methylmagnesium bromide in 1 l. of ether. When the addition was complete, 200 ml. of concd. hydrochloric acid was added, the organic layer was separated and the solvent was removed in a vacuum. Distillation through a 25 mm. × 90 cm. column packed with Heli-pak resulted in 74.5 g. (86.6% yield) of heptyltrimethylsilanes, b.p. 180–183°, $n^{25}{}_D$ 1.4222 to 1.4170, $d^{25}{}_4$ 0.7566 to 0.7491; found *R*D 0.377–0.336, calcd. *R*D 0.338.

Anal. Calcd. for $SiC_{10}H_{24}$: Si, 16.28. Found: Si, 16.53.

A gas-liquid phase chromatogram of a typical fraction (b.p. 180°, $n^{25}{}_D$ 1.4222, $d^{25}{}_4$ 0.7566) revealed that three components were present. The major component was identical with an authentic sample of *n*-heptyltrimethylsilane, and the two minor components were identical with a mixture of authentic 3- and 4-heptyltrimethylsilanes.

Authentic *n*-Heptyltrimethylsilane.—To a vigorously stirred dispersion of 46 g. (2 moles) of sodium in 500 ml. of dry boiling toluene and 25 g. of trimethylchlorosilane was slowly added a mixture of 134 g. (1 mole) of *n*-heptyl chloride and 108.5 g. (1 mole) of trimethylchlorosilane. After the addition was complete the mixture was refluxed for 30 minutes, washed with 500 ml. of water, and the solvent was removed under reduced pressure. The residue was refluxed for 16 hours with 100 ml. of 10% alcoholic potassium hydroxide, and most of the alcohol was removed under reduced pressure. The residue was then washed with water, cold concentrated sulfuric acid and finally with water. After drying over anhydrous sodium sulfate the product was distilled through a 15 × 800 mm. vacuum-jacketed column packed with Heli-pak to give 77.5 g. (45% yield) of *n*-heptyltrimethylsilane, b.p. 184° at 750 mm., $n^{25}{}_D$ 1.4186, $d^{25}{}_4$ 0.7466; found *R*D 0.338, calcd. *R*D 0.338.[2] A gas-liquid phase chromatogram of the product detected no impurities.

Anal. Calcd. for $SiC_{10}H_{24}$: Si, 16.28. Found: Si, 16.37.

3- and 4-Heptyltrichlorosilane.—To a refluxing solution of 98 g. (1 mole) of heptene-3 and 406.5 g. (3 moles) of trichlorosilane was added 40 g. of a 25% solution of acetyl peroxide in dibutyl phthalate over a period of 5 days. Distillation resulted in 110 g. (47% crude yield) of the 3- and 4-heptyltrichlorosilanes. Redistillation through a 15 × 800 mm. vacuum jacketed column packed with Heli-pak gave 3- and 4-heptyltrichlorosilane, b.p. 205–206° at 750 mm., $n^{25}{}_D$ 1.4510, $d^{25}{}_4$ 1.103; found *R*D 0.244, calcd. *R*D 0.244.

Anal. Calcd. for $SiC_7H_{15}Cl_3$: neut. equiv., 77.8; Si, 12.04. Found: neut. equiv., 80.0; Si, 11.72.

3- and 4-Heptyltrimethylsilane.—To a solution of one mole of methylmagnesium bromide in 500 ml. of ether was added slowly 58 g. (0.25 mole) of the pure 3- and 4-heptyltrichlorosilane with stirring. The product was isolated in the usual manner and distilled through a 15 × 800 mm. vacuum jacketed column packed with Heli-pak, to give 26.0 g. (60.2% yield) of 3- and 4-heptyltrimethylsilane, b.p. 174.5–176° at 750 mm., $n^{25}{}_D$ 1.4262–1.4258, $d^{25}{}_4$ 0.7622–0.7620; found *R*D 0.336, calcd. *R*D 0.338.

Acknowledgments.—The authors wish to express their appreciation to Cynthia Ann Skelton for carrying out the chromatographic analysis and to Janet Gardner for carrying out some of the preparative work.

MIDLAND, MICHIGAN

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1-Oxa-2-Silacycloalkanes and their Conversion to Bis-(hydroxyalkyl)-disiloxanes

BY W. H. KNOTH, JR., AND R. V. LINDSEY, JR.

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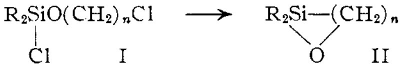
Four 2,2-disubstituted 1-oxa-2-silacycloalkanes, members of a new class of silicon heterocycles, have been prepared by ring closure of the corresponding (chloroalkoxy)-chlorosilanes. The latter were made from dichlorosilanes and α,ω-chlorohydrins or oxacycloalkanes. The oxasilacycloalkanes were hydrolyzed readily to α,ω-bis-(hydroxyalkyl)-disiloxanes.

In studies of heterocyclic silicon chemistry, several 2,2-disubstituted 1-oxa-2-silacycloalkanes (II) have been prepared by heating the corresponding (chloroalkoxy)-chlorosilanes (I) with metallic sodium or lithium.



a, R = CH_3, *n* = 3; c, R = CH_3, *n* = 4
b, R = C_6H_5, *n* = 3; d, R = CH_3, *n* = 5

The (chloroalkoxy)-chlorosilanes were obtained by two routes. Those in which *n* = 3 were obtained from the appropriate disubstituted dichlorosilane and trimethylene chlorohydrin with triethylamine as acid acceptor. Compounds in which *n* = 4 and 5 were prepared smoothly and in good yields by heating the dichlorosilanes with tetrahydrofuran and tetrahydropyran, respectively, to 200° in an autoclave.[1] At 250°, tetrahydro-

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(1) W. I. Patnode and R. O. Sauer, U. S. Patents 2,381,137 (August