having bands at 2150–2050 cm.$^{-1}$ due to C–D stretching vibrations, was transparent from 1443 to 1387 cm.$^{-1}$ indicating the absence of a CH_2 group adjacent to a carbonyl[7] and revealed a band at 1038 cm.$^{-1}$ which has been assigned to a CD_2 scissoring vibration at C-16 in a 17-keto steroid.[8]

Anal. Calcd. for $C_{19}H_{22}D_6O_2$: D, 21.43 atom % excess. Found: D, 20.30, 20.40 atom % excess (5.7 atoms D).

The Bromination of 2,2,4,4,16,16-Hexadeuterio-5α-androstane-3,17-dione.—2,2,4,4,16,16-Hexadeuterio-5α-androstane-3,17-dione (114.5 mg., 0.389 mmole) containing 5.7 atoms of deuterium and 1.0 ml. of a bromine–sodium acetate–acetic acid solution containing 0.348 mmole of bromine and 0.58 mmole of sodium acetate/ml. of solution, were placed in a 10-ml., round-bottom stoppered flask and stirred magnetically at ambient temperature for 84 hr. The reaction was terminated with some bromine still present by pouring it into 35 ml. of chilled saturated sodium chloride solution. The orange precipitate was collected by filtration, washed with 2% sodium bicarbonate solution and then water, and air dried on the filter for 2 hr. until the orange color disappeared. The filter cake was dissolved in acetone, the solution was filtered to remove sodium chloride, and the solvent was removed at the aspirator to give 130 mg. of a tan solid. Thin layer chromatography of this product was carried out on two 1-mm.-thick silica gel plates in a 30% ethyl acetate–benzene solvent system. Development of side bands with 2,4-dinitrophenylhydrazine reagent indicated the presence of three zones: dibromoandrostane-3,17-dione, 2α-bromoandrostane-3,-17-dione, and unreacted starting ketone. The monobromo zone was separated from the plates and the compound eluted from the silica gel with acetone. Removal of the solvent gave 36.7 mg. of deuterated 2α-bromoandrostane-3,17-dione, 25.4% yield. One recrystallization from acetone–hexane yielded 31 mg. of white crystals: m.p. 192–195°; λ_{max}^{KBr} 1736, 1712, 1433, and 1379 cm.$^{-1}$. Authentic nondeuterated 2α-bromoandrostane-3,17-dione had m.p. 204.5–206°; λ_{max}^{KBr} 1733, 1712, 1433, 1403, and 1376 cm.$^{-1}$. The n.m.r. spectra of both the deuterated and nondeuterated compounds, taken at the same concentration, revealed a quartet centered at τ 5.23 due to the 2β-proton ($J_{1\beta,2\beta} = 6.5$ c.p.s. and $J_{1\alpha,2\beta} = 13.5$ c.p.s.). Comparison of the areas under these quartets indicated that, in the deuterated compound, the quartet represented 0.58 atom of hydrogen or 42% deuterium in the 2β position.

In another experiment, terminated after 46 hr., where the work-up excluded the bicarbonate wash and air drying period, the monobromo product was obtained in 14% yield. The n.m.r. analysis indicated 43% deuterium in the 2β position.

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The Addition of Silicon Hydrides to Olefinic Double Bonds. XI. Exchange of Methyl and Trimethylsiloxy Groups in Bistrimethylsiloxymethylsilane

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During the addition of bistrimethylsiloxymethylsilane to hexene-2 in the presence of chloroplatinic acid a methyl–trimethylsiloxy exchange in bistrimethylsiloxymethylsilane occurred so that the products formed included those expected from pentamethyldisiloxane

$$2(Me_3SiO)_2SiMeH \longrightarrow Me_3SiOSiMe_2H + (Me_3SiO)_3SiH$$

and tristrimethylsiloxysilane. No example has been observed previously of such a reaction under the mild conditions of these experiments.

A study of the addition of bis(trimethylsiloxy)methylsilane [I, $(Me_3SiO)_2SiMeH$], to hexene-2 in the presence of chloroplatinic acid revealed a most unexpected side reaction. An exchange of methyl and trimethylsiloxy groups occurred in a way never before observed under such mild conditions (<138°).

Up to this time the rupture of silicon–alkylcarbon bonds has been observed to occur only under vigorous conditions. For example, Eaborn[1] discusses the redistribution of chloromethylsilanes at temperatures between 250 and 400° under pressure, preferably in the presence of aluminum chloride.

Ryan[2] has reported the redistribution of alkylalkoxysilanes at temperatures in the range of 250° in the presence of catalytic amounts of a strong base. It was therefore surprising to find that methyl–silicon bonds had been broken when the temperature was less than 140° and the mole ratio of chloroplatinic acid to bistrimethylsiloxymethylsilane was 5×10^{-5}.

The addition of bistrimethylsiloxymethylsilane to hexene-2 in the presence of chloroplatinic acid yielded the expected product, bistrimethylsiloxymethylhexylsilane, eq. 1. Tristrimethylsiloxysilane, hexylpentamethyldisiloxane, and 3,5-bistrimethylsiloxyoctamethyltetrasiloxane [$(Me_3SiO)_2SiMeOSiMe(OSiMe_3)_2$] were also formed as by-products of the reaction.

$$\underset{\text{I}}{(Me_3SiO)_2SiMeH} + \text{hexene-2} \longrightarrow \underset{\text{II}}{(Me_3SiO)_2SiMeHex} \qquad (1)$$

The only plausible explanation for the existence of the first two by-products requires an intermolecular methyl–trimethylsiloxy exchange according to eq. 2. Tristrimethylsiloxysilane does not add to hexene-2 under the conditions of the experiment. The third by-product, $[(Me_3SiO)_2SiMe]_2O$, is the oxidation product of I.

$$\begin{tikzcd}
2(Me_3SiO)_2SiMeH \arrow[r, "Pt", "\text{hexene-2}"'] & Me_3SiOSiMe_2H \arrow[d, "\text{hexene}"] & + (Me_3SiO)_3SiH \\
 & Me_3SiOSiMe_2Hex & (2)
\end{tikzcd}$$

The experiment was repeated twice to check the reproducibility of the reaction. In all cases the results were identical.

The purity and identity of each reagent were carefully checked. The unexpected products cannot be ascribed to impurities in the reagents.

At the present time little is known of the scope of the rearrangement reaction or the specific conditions which will permit its occurrence.

The use of cyclohexene instead of hexene-2 under the same conditions apparently leads to comparable results as followed by vapor phase chromatography. However, no similar rearrangements could be detected with hexene-1 and bistrimethylsiloxymethylsilane, nor with pentamethyldisiloxane and either hexene-1 or hexene-2.

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[1] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p. 68.

[2] J. W. Ryan, *J. Am. Chem. Soc.*, **84**, 4730 (1962).

Experimental

Vapor phase chromatographic (v.p.c.) analyses were performed using a stainless steel column 4 ft. long by 0.25 in. in diameter packed with 23% Dow Corning 200 silicone gum rubber on Chromosorb W. H^1 n.m.r. spectra were obtained on Varian Associates Model A-60 spectrometer at a radiofrequency of 60 Mc./sec. with carbon tetrachoride as a solvent and 1% of tetramethylsilane as an internal standard.

Preparation of Standards and Reagents.—Pentamethyldisiloxane was a Dow Corning Corporation product carefully redistilled having the properties: b.p. 85° at 750 mm., n^{25}_D 1.3715, d^{25}_4 0.7546, R_D[3] 0.3008 (calcd. 0.3000).

Bistrimethylsiloxymethylsilane was prepared by the acid equilibration of hexamethyldisiloxane (2750 g., 16.9 moles) and 2,4,6,-8,10-pentamethylcyclopentasiloxane (359 g., 5.97 equiv.). The mixture was stirred and heated at 60° for 9 hr., filtered, and distilled to give bistrimethylsiloxymethylsilane: 735 g., 55.3% yield, b.p. 66° at 59 mm., n^{25}_D 1.3800, d^{25}_4 0.8136, R_D 0.2847 (calcd., 0.2841). The literature[4a] reports b.p. 142° at 760 mm., n^{20}_D 1.3818, d^{20}_4 0.8194.

Anal. Calcd. for $(Me_3SiO)_2MeSiH$: Si, 37.85; SiH, 0.449. Found: Si, 37.95; SiH, 0.453.

Tristrimethylsiloxysilane was prepared by the hydrolysis of a mixture of trichlorosilane and trimethylchlorosilane in isopropyl alcohol, b.p. 85° at 30 mm., n^{25}_D 1.3846. The literature[4b] reports b.p. 67–68° at 11 mm., n^{20}_D 1.3860, d^{20}_4 0.854.

Anal. Calcd. for $(Me_3SiO)_3SiH$: Si, 37.9; SiH, 0.338. Found: Si, 37.8; SiH, 0.326.

The H^1 n.m.r. spectrum of this compound is two singlets with τ-values of 9.88 and 5.75 with integrated values of 27.3/1.0 (calcd. 27/1).

The hexenes were obtained from The Phillips Petroleum Co. and were at least 95% pure.

The Addition of Pentamethyldisiloxane to Hexene-1.—In a 300-ml. flask fitted with a condenser were placed pentamethyldisiloxane (14.8 g., 0.100 mole), hexene-1 (8.4 g., 0.10 mole), and 0.05 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. The reaction began at 45° and apparently was complete in less than 1 min. The temperature rose to 95° although the flask was cooled in a pan of cold water. Distillation yielded hexylpentamethyldisiloxane: 15.2 g., 66.1% yield, b.p. 198° at 750 mm., n^{25}_D 1.4087, d^{25}_4 0.7926, R_D 0.3117 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

Anal. Calcd. for $C_{11}H_{28}OSi_2$: Si, 24.2. Found: Si, 24.46.

The Addition of Pentamethyldisiloxane to Hexene-2.—In a 200-ml. flask fitted with a condenser were placed pentamethyldisiloxane (14.8 g., 0.100 mole), hexene-2 (8.4 g., 0.10 mole), and 0.05 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. After heating for a total of 30 hr. the temperature had risen to 135°. Distillation yielded hexylpentamethyldisiloxane: 11.3 g., 48.7% yield, b.p. 200° at 750 mm., n^{25}_D 1.4075, d^{25}_4 0.7971, R_D 0.3095 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

No products that might have formed by a methyl–trimethylsiloxy rearrangement were detected by v.p.c. in these experiments.

Anal. Calcd. for $C_{11}H_{28}OSi_2$: C, 56.8; H, 12.14; Si, 24.2. Found: C, 56.8; H, 12.4; Si, 24.24.

The adducts of hexene-1 and hexene-2 to pentamethyldisiloxane would be expected to have slightly different physical properties because different hexyl isomers or combinations of hexyl isomers may be present.[5]

The Addition of Bistrimethylsiloxymethylsilane to Hexene-2.—In a 2-l., one-necked flask vented *via* a condenser and calcium chloride tube were placed bistrimethylsiloxymethylsilane (222 g., 1.00 mole), hexene-2 (84.2 g., 1.00 mole), and 0.50 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. The highest temperature reached while heating for a period of 10 hr. was 138°. Periodic v.p.c. analyses indicated the continuous formation of adduct and rearrangement products, and a 95% conversion after 10 hr. of heating. Distillation yielded these products.

A.—Bistrimethylsiloxymethylhexylsilane (137 g., 56.6% yield) had b.p. 70° at 5 mm., n^{25}_D 1.4071, and was partially separated into two components by v.p.c., indicating the presence of at least two isomers.[5] Bistrimethylsiloxymethylhexylsilane prepared in this manner has the following physical properties and analyses: b.p. 70° at 5 mm., n^{25}_D 1.4070, d^{25}_4 0.8320, R_D 0.2959 (calcd. for $(Me_3SiO)_2SiMeHex$, 0.2961).

Anal. Calcd. for $C_{13}H_{34}O_2Si_3$: Si, 27.5. Found: Si, 27.44.

B.—Tristrimethylsiloxysilane (21.5 g., 0.0726 mole), 14.5% yield with a purity of 95%, had b.p. 69° at 14 mm., n^{25}_D 1.3850, d^{25}_4 0.8407, R_D 0.2788 [calcd. for $(Me_3SiO)_3SiH$, 0.2818].

This product had identical H^1 n.m.r. and infrared spectra and v.p.c. retention times with the standard.

Anal. Calcd. for $(Me_3SiO)_3SiH$: Si, 37.9; SiH, 0.338. Found: Si, 36.9, 37.2; SiH, 0.322, 0.353.

C.—Hexylpentamethyldisiloxane (14.5 g., 0.0625 mole), 12.5% yield, with a purity of 96%, had b.p. 201° at 750 mm., n^{25}_D 1.4080, d^{25}_4 0.8026, R_D 0.3074 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

Anal. Calcd. for $C_{11}H_{28}OSi_2$: C, 56.8; H, 12.14; Si, 24.15. Found: C, 55.96, 56.46; H, 12.58, 12.31; Si, 24.50.

The H^1 n.m.r. and infrared spectra as well as the v.p.c. retention time for this sample were indistinguishable from those of the product obtained from pentamethyldisiloxane and hexene-2.

D.—3,5-Bistrimethylsiloxyoctamethyltetrasiloxane (15.2 g., 6.4%) with a purity of 95% had b.p. 95° at 3 mm., n^{25}_D 1.3961, d^{25}_4 0.8838, R_D 0.2719 [calcd. for $(Me_3SiO)_2MeSiOSiMe(OSiMe_3)_2$, 0.2697]. Literature[6] values given are b.p. 256°, n^{20}_D 1.3947, d^{20}_4 0.893.

Anal. Calcd. for $C_{14}H_{42}O_5Si_6$: C, 36.7; H, 8.79; Si, 36.75. Found: C, 39.02, 39.40; H, 9.21; Si, 34.94, 34.98.

The infrared spectrum was identical with that of a standard of $[(Me_3SiO)_2SiMe]_2O$. H^1 n.m.r. analysis revealed the presence of two types of methyl protons in the ratio of six to one, which is correct for the proposed structure.

The Attempted Addition of Tristrimethylsiloxysilane to Hexene-2.—A solution consisting of tristrimethylsiloxysilane (50.0 g., 0.169 mole), hexene-2 (14.2 g., 0.169 mole), and 0.17 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol was heated at reflux (108°) for 7 days. During the period of heating an additional 0.17 ml. of catalyst was added. Vapor phase chromatography indicated the amount of adduct formation (if any) to be less than 5%.

The Addition of Bistrimethylsiloxymethylsilane to Cyclohexene.—A solution of bistrimethylsiloxymethylsilane (22.2 g., 0.100 mole), cyclohexene (8.3 g., 0.10 mole), and 0.05 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol was heated at reflux for 4 days, at which time v.p.c. analysis showed a 90% conversion. The highest temperature attained was 150°. The products from the reaction were not isolated, but v.p.c. analysis of the solution showed a pattern that was almost identical with the curve of the addition of bistrimethylsiloxymethylsilane to hexene-2. Two of the products, however, were identified by their retention times as being $(Me_3SiO)_3SiH$ and $[(Me_3SiO)_2MeSi]_2O$.

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(3) Specific refractions calculated by means of the bond refractions of A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

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(5) H. M. Bank, J. C. Saam, and J. L. Speier [*J. Org. Chem.*, **29**, 792 (1964)] have recently reported that *sym*-tetramethyldisiloxane and hexene-2 form a mixture of 1-, 2-, and 3-hexyl isomers.

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Preparation of *cis*-Cyclododecene, Cyclododecyne, and Cyclododecanone

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The *cis* isomer of cyclododecene (II) is now readily accessible by means of the diimide reduction of butadiene trimer, *trans,trans,cis*-1,5,9-cyclododecatriene (I), as recorded by Ohno and Okamoto very recently.[1] The same reaction has been observed independently in this laboratory and the details of our procedure will be given in the Experimental section. The present paper

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(1) M. Ohno and M. Okamoto, *Tetrahedron Letters*, 2423 (1964).