Stereochemistry of Methyldichlorosilane Additions to Pentadienes[1]

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The reaction of methyldichlorosilane with *cis*-1,3-, *trans*-1,3-, and 1,4-pentadienes in the presence of chloroplatinic acid has been investigated. All products were converted into the trimethylsilyl derivatives for glpc analysis and identification purposes. In the reaction involving 1,4-pentadiene, three products were found in a 75.5% yield with the following composition after methylation: 1-trimethylsilyl-4-pentene (87.2%); *cis*-1-trimethylsilyl-2-pentene (9.3%); and *cis*-1-trimethylsilyl-3-pentene (3.5%). The reaction with *trans*-1,3-pentadiene gave three products in a 74.6% yield with the following composition after methylation: *cis*-1-trimethylsilyl-2-pentene (42.0%); *trans*-2-trimethylsilyl-3-pentene (39.1%); and *trans*-1-trimethylsilyl-2-pentene (18.9%). The reaction of *cis*-1,3-pentadiene gave five products in a 82.2% yield, with the following composition after methylation: 1-trimethylsilyl-4-pentene (1.3%); *cis*-1-trimethylsilyl-2-pentene (23.2%); *cis*-1-trimethylsilyl-3-pentene (60.8%); *trans*-2-trimethylsilyl-3-pentene (10.5%); and *trans*-1-trimethylsilyl-2-pentene (4.2%). A mechanism accounting for the products is proposed. This involves a platinum–diene–silane complex which then gives the various products. Besides 1,2 addition, in which silicon is found in the 1 position, reverse 1,2 addition, in which silicon is bonded to the 2 position, and 1,4 addition with silicon in the 1 position occur. This reverse 1,2 addition is accounted for by the stabilizing effect of the second double bond, and the predominance of cis products resulting from 1,4 addition is thought to be due to the original diene reacting in the cisoid conformation.

Though platinum and chloroplatinic acid catalyzed[1–8] additions and thermally induced[9] additions of silanes to dienes have been reported previously, the influence of systematic changes in the structure of the diene on the stereochemistry of the reaction has not been determined. The addition of methyldichlorosilane to *cis*-1,3-, *trans*-1,3-, and 1,4-pentadiene using chloroplatinic acid as a catalyst was therefore undertaken.

The addition of silanes to simple olefins and acetyllenes, using a chloroplatinic acid catalyst, has revealed some unique properties of this catalyst system. Silicon hydrides add to 1-alkenes in such a way that the silicon becomes attached to the terminal position, and the hydrogen adds to the internal portion of the double bond.[10] If the double bond is internal, as in 2-pentene, it has been shown that migration often occurs, with silicon again being bonded to the terminal carbon atom.[10] In the case of acetylenes, silanes add in a cis manner and no bond migration takes place.[11] Optically active silanes have been added to double and triple bonds,[12] and, in the cases studied to date, the silane retains its optical activity.

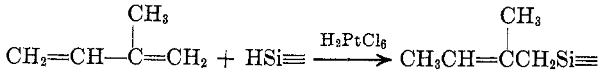
The additions of methyldichlorosilane to the pentadienes were carried out in cyclohexane solvent using catalytic amounts of an isopropyl alcohol solution of chloroplatinic acid. Methyldichlorosilylpentenes were generally obtained in high yields and then methylated for glpc analysis.

$$n\text{-}C_5H_8 + CH_3SiCl_2H \xrightarrow{H_2PtCl_6} CH_3Cl_2SiC_5H_9 \xrightarrow[CH_3MgBr]{CH_3MgCl \text{ or}} (CH_3)_3SiC_5H_9$$

Since the reactions may involve migration as well as 1,2 and 1,4 additions to the diene system, as many as 16 isomers are possible. The reaction was found to be much more stereoselective than this (see Table I), and there were never more than five product isomers.

For the nonconjugated 1,4-pentadiene, simple addition to one of the double bonds, followed by methylation, leads to the principal reaction product 1-trimethylsilyl-4-pentene (**1**). This was shown to be identical with 1-trimethylsilyl-4-pentene prepared by an independent method.[13] The mode of addition is comparable to that reported by Vdovin and Petrov[4] for chloroplatinic acid catalyzed addition of methyldichlorosilane to 1,5-hexadiene, and the platinum-catalyzed addition of trichloro- and triethylsilane to 1,5-cyclooctadiene.[3]

Previous reports on the addition of silanes to conjugated dienes have involved 1,4 addition. Bailey and Pines[2] prepared 1-trichlorosilyl-2-butene by the platinum-catalyzed reaction of trichlorosilane with butadiene, and Mironov and Nepomnina[8] obtained 43% of 2-methyldichlorosilyl-3-pentene by 1,4 addition to 1,3-pentadiene using chloroplatinic acid catalyst. Similarly, the additions of silanes to isoprene[6] have been found to occur by the 1,4 mode of addition.



$$CH_2{=}CH{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + HSi{\equiv} \xrightarrow{H_2PtCl_6} CH_3CH{=}\overset{\overset{CH_3}{|}}{C}CH_2Si{\equiv}$$

Using *cis*- and *trans*-1,3-pentadiene, we have found that both simple and conjugate addition occurs with methyldichlorosilane and chloroplatinic acid.

trans-1,3-Pentadiene gives three monoadducts upon reaction with methyldichlorosilane catalyzed by chloroplatinic acid, as shown by the isolation and characterization of the methylated products.

Structure **2** would be obtained from 1,4 addition to the s-cis form of *trans*-1,3-pentadiene. The struc-

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[1] Taken from the Ph.D. Thesis of C. Zullig, University of Detroit, 1969.

[2] D. L. Bailey and A.N. Pines, *Ind. Chem.*, **46**, 2363 (1954).

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[8] V. F. Mironov and V. V. Nepomnia, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1419 (1960).

[9] (a) C. R. Kreugar, *Int. Symp. Organosilicon Chem., Sci. Commun.*, 74 (1965); *Chem. Abstr.*, **65**, 8944*d* (1966). (b) R. M. Pike and P. M. McDonagh, *J. Chem. Soc.*, 2831 (1963). (c) M. G. Voronkov and N. G. Romanova, *Zh. Obshch. Khim.*, **28**, 2122 (1958); *Chem. Abstr.*, **53**, 2075*d* (1959).

[10] J. L. Speier, J. A. Webster, and G. A. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

[11] R. A. Benkeser, M. L. Burrows, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, **83**, 4385 (1961).

[12] L. H. Sommer, K. W. Michael, and H. Fujimoto, *J. Amer. Chem. Soc.*, **89**, 1519 (1967).

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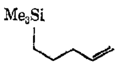
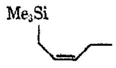
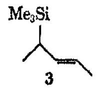
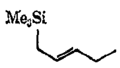
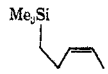
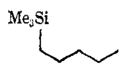
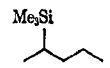
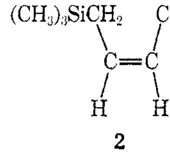
TABLE I

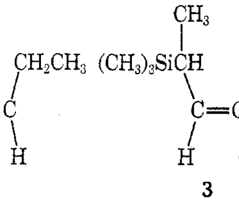
TRIMETHYLSILYLPENTENES PRODUCED FROM THE PENTADIENES AND THEIR HYDROGENATION PRODUCTS[a]

Registry no.	Pentadiene	Addition, %	Methylated product composition, %					Hydrogenation products, %	
			 **1**	 **2**	 **3**	 **4**	 **5**		
591-93-5	1,4-	75.5	87.2	9.3			3.5	97.7	2.3
2004-70-8	*trans*-1,3-	74.6		42.0	39.1	18.9		62.6	37.4
1574-41-0	*cis*-1,3-	82.2	1.3	23.2	10.5	4.2	60.8	91.1	8.9

[a] Results cited are area per cent from glpc analysis on a 26-ft UCON Polar column.



2



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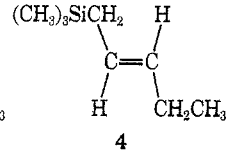


4

ture was confirmed by independent synthesis. Product **4** would also result from 1,4 addition, and was identified by comparison with an independently synthesized sample. The simple 1,2 addition probably accounts for the *trans*-2-trimethylsilyl-3-pentene (**3**), since the original geometry of the double bond in *trans*-1,3-pentadiene is preserved. The appearance of the silyl group at the second carbon is somewhat surprising in view of the work by Speier, Webster, and Barnes[10] which shows a strong preference of the silyl group for the terminal position. However, Musolf and Speier[14] have shown that silane additions to phenylalkenes produce two products, one with silicon at the terminal position of the alkyl group, and the other with the silicon α to the aromatic ring. The preference of the silicon atom for a carbon α to a center of unsaturation would seem to be the most important factor in the formation of **3**.

$$\begin{array}{l} C_6H_5(CH_2)_nCH{=}CH_2 + HSi{\equiv} \\ \quad\text{or} \\ C_6H_5CH{=}CH(CH_2)_nH \\ \quad n = 0 \text{ to } 4 \end{array} \xrightarrow{H_2PtCl_6} \begin{array}{c} C_6H_5(CH_2)_nCH_2CH_2Si{\equiv} \\ + \\ C_6H_5\underset{\displaystyle Si{\equiv}}{\underset{|}{C}}H(CH_2)_nCH_3 \end{array}$$

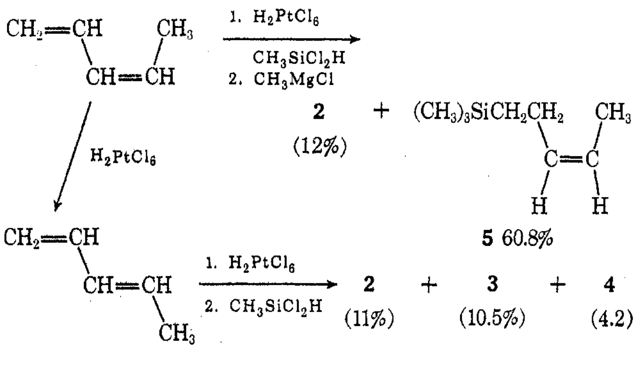
The addition to *cis*-1,3- pentadiene was somewhat more complex, as five different products resulted, and, when an excess of diene was employed, 11.8% isomerization of the unreacted diene to the *trans*-1,3-pentadiene was detected (see Table II). This isomerization was negligible in the cases of the other two dienes. If it is assumed that some of the products (Table I) from the *cis*-1,3-pentadiene arise from the *trans*-1,3-pentadiene produced by isomerization, an approximate product composition due solely to the cis isomer can be determined. *trans*-2-Trimethylsilyl-3-pentene (**3**) should only be produced by 1,2 addition to the *trans*-1,3-pentadiene. On this basis 11% of compound **2** and all of compound **4** can be accounted for by the isomerization of the starting diene. The origin of **1** is not known, but it amounts to only 1.3% of the product. The major product, *cis*-1-trimethylsilyl-3-pentene (**5**), is due to simple 1,2 addition to the terminal double bond, while **2** would be due to 1,4 addition to the s-cis form of the diene.

TABLE II

ISOMERIZATION OF PENTADIENES CONCURRENT WITH ADDITION[a]

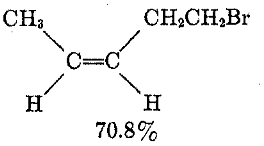
Starting diene	Addition product yield, %	Isomerized pentadiene % composition 1,4-	*cis*-1,3-	*trans*-1,3-
1,4-	22.9	93.8	1.9	4.3
cis-1,3-	19		88.2	11.8
trans-1,3-	72.5		1.1	98.9

[a] Excess pentadiene analyzed by glpc after 24 hr at 58° with chloroplatinic acid, methyldichlorosilane, and cyclohexane. See Experimental Section for details.



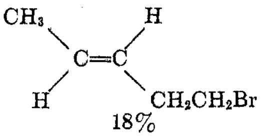
All of the trimethylsilylpentenes formed by addition to the pentadienes were prepared by independent methods with the exception of **3**. Hydrogenation of the trimethylsilylpentenes produced by addition to *trans*-1,3-pentadiene yielded only 1- and 2-pentyl-

$$CH_3CH_2C{\equiv}CCH_2Br + (CH_3)_3SiCl \xrightarrow{Mg} CH_3CH_2C{\equiv}CCH_2Si(CH_3)_3 \xrightarrow[PtO_2]{H_2} \mathbf{2}$$



70.8%

and + (CH₃)₃SiCl $\xrightarrow{Mg}$ **4** (20%) + **5** (79%) in 30.7% yield



18%

$$CH_2{=}CHCH_2CH_2Br \xrightarrow[3.\ CH_3MgCl]{1.\ Mg\quad 2.\ SiCl_4} \mathbf{1}$$

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[14] M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964).

trimethylsilanes (62.6 and 37.4%, respectively). The 2-pentyltrimethylsilane was shown to be derived from **3**, since separate hydrogenation of **2**, the only other possible source, yielded only 1-pentyltrimethylsilane. Product **3** was further characterized by nmr and ir spectra where a band at 1005 cm^{-1}, characteristic of trans olefins, was evident. All attempts to synthesize **3** independently were unsuccessful. The other adducts (**1**, **2**, **4**, and **5**), in addition to having glpc retention times identical with those of the authenic samples, produced nmr, ir, and hydrogenation data consistent with the structures given.

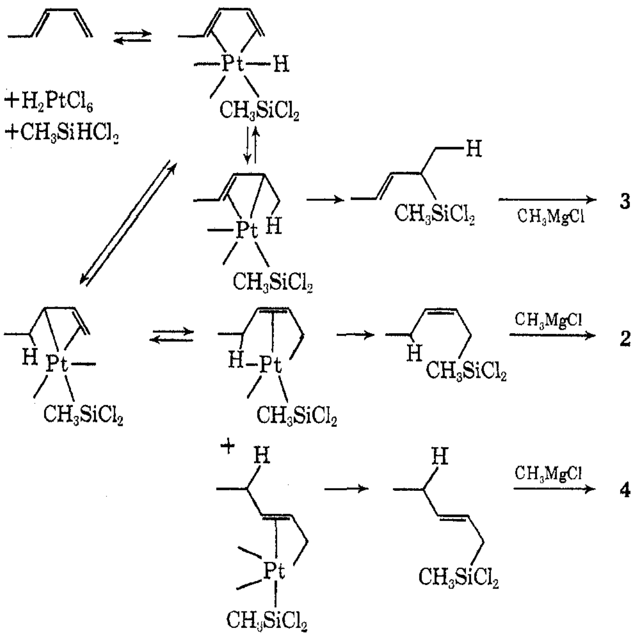
In order to exclude, if possible, any prior isomerization of the diene, an excess of each pentadiene was used for the additions of methyldichlorosilane. The unreacted pentadiene after 24 hr under reaction conditions was analyzed by glpc. The results are summarized in Table II. Only the *cis*-1,3-pentadiene shows significant isomerization and some part of the addition products may arise from the *trans*-1,3-pentadiene produced in the isomerization. Isomerization of the adducts was not significant, since varying the time between completion of the reaction and the work-up of the reaction mixture did not change the product composition. In addition, each diene produced a distinctive product composition, so that isomerization toward any kind of equilibrium composition can be ruled out.

There is little selectivity in the reaction of the methyldichlorosilylpentenes with methylmagnesium chloride, so that analysis of the trimethylsilypentenes, which are more convenient to handle, gave good results. For example, a mixture of three methyldichlorosilylpentenes (in the ratio 1.08:1:0.74) produced in a competition reaction between *cis*- and *trans*-1,3-pentadiene gave the corresponding trimethylsilylpentenes in the ratio 1.11:1:0.67. This competition reaction, in which 0.1 mol of *cis*-1,3-pentadiene and 0.1 mol of *trans*-1,3-pentadiene were allowed to compete for 0.1 mol of methyldichlorosilane, demonstrated the more rapid reaction of the *trans*-1,3-pentadiene since only 27.6% of the unreacted *trans*-1,3-pentadiene remained while 72.4% of *cis*-1,3-pentadiene was left.

Chalk and Harrod[15] have formulated a mechanism for platinum-catalyzed additions of silanes to olefins which accounts for the isomerization and terminal silane addition often observed with nonterminal olefins.[10,16-18] A similar mechanism can account for the results of methyldichlorosilane addition to pentadienes using chloroplatinic acid, although both double bonds of the conjugated pentadienes must sometimes be involved in the platinum complex to account for the stereoselectivity of the addition and the major amounts of 1,4 addition found. The involvement of dienes, as bidentate ligands, in platinum-catalyzed silane additions has been proposed by Kuivila and Warner[7] for the rigid bicycloheptadiene system and probably occurs in other chloroplatinic acid catalyzed additions to dienes.[19] In fact, stable Pt(II)–diene complexes have been prepared,[20-22] although no attempt was made to add silanes.

The addition products of methyldichlorosilane which involve only the terminal double bond, **1** for 1,4-pentadiene, **3** for *trans*-1,3-pentadiene, and **5** for *cis*-1,3-pentadiene, can be accounted for by a simple platinum–olefin complex. The large amount of simple 1,2 addition and the small amount of conjugate or 1,4 addition for the *cis*-1,3-pentadiene as compared to *trans*-1,3-pentadiene must result from differences in the s-cis form of the diene, which is apparently preferred for the platinum–diene complex. The terminal methyl group must either interfere with the coplanarity of the s-cis form of diene, which may be a requirement for stable complex formation, or prevent the close approach of the platinum. Chatt[20,21] has shown that, in general, Pt(II)–diene complexes are more stable than Pt(II)–olefin complexes but that there are differences among dienes that must be ascribed to the geometry of the system. The competition between *cis*-1,3-pentadiene and *trans*-1,3-pentadiene for methyldichlorosilane further illustrates the difficulty in forming a diene complex with *cis*-pentadiene, since 72% of the *trans*-1,3-pentadiene was transformed into products but only 28% of the *cis*-1,3-pentadiene reacted with the methyldichlorosilane.

A basic mechanism that can account for the 1,2- and 1,4-addition products of *trans*-1,3-pentadiene can be written in the following way.



The importance of the s-cis or cisoid form can be seen for the *trans*-1,3-pentadiene, and the reluctance of the *cis*-1,3-pentadiene to assume this form during reaction has also been demonstrated. The 1,4-pentadiene yields some isomerized product which may arise from addition to a cyclic complex or just as likely from isomerization of the diene prior to addition.

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[15] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

[16] J. C. Saam and J. L. Speier, *J. Amer. Chem. Soc.*, **80**, 4104 (1958).

[17] T. G. Selin and R. West, *J. Amer. Chem. Soc.*, **84**, 1863 (1962).

[18] R. A. Benkeser, S. Dunny, G. S. Li, P. G. Nerlekar, and S. D. Work, *J. Amer. Chem. Soc.*, **90**, 1871 (1968).

[19] R. H. Fish and H. G. Kuivila, *J. Org. Chem.*, **31**, 2445 (1966).

[20] J. Chatt and R. G. Wilkens, *J. Chem. Soc.*, 2622 (1952).

[21] J. Chatt, *J. Chem. Soc.*, 2496 (1957).

[22] E. W. Abel, M. A. Bennet, and G. Wilkenson, *J. Chem. Soc.*, 3178 (1959).

Experimental Section

All the pentadienes were obtained from Chemical Samples Co. and were shown to be better than 99% pure by glpc analysis. Routine glpc work was done on a Varian Aerograph Model A-90P gas chromatograph using a 26 ft × 0.25 in. 15% UCON Polar on 60–80 mesh firebrick column (column A) and 28 ft × 0.50 in. preparative column of 15% UCON Polar on 30–60 mesh firebrick (column B). Separation and identification of isomers were further checked using a 0.125 in. diameter, 300 ft Perkin-Elmer 1050 capillary column coated with Apiezon (column C) on a Perkin-Elmer 800 gas chromatograph. Infrared spectra were obtained using a Beckman IR-5, a Beckman IR-12, and a Perkin-Elmer Model 337. The nmr spectra were taken on a Varian A-60A.

Addition of Methyldichlorosilane to 1,4-Pentadiene.—A mixture of 25 ml of cyclohexane and 50 μl of 0.2 *M* chloroplatinic acid (in isopropyl alcohol) was stirred while an equal molar mixture of 20 ml (13.6 g, 0.20 mol) of 1,4-pentadiene and 21.0 ml (23.0 g, 0.20 mol) of methyldichlorosilane was added dropwise. Approximately 15 min after the addition was completed, an exothermic reaction took place and the temperature rose to 93°. After the initial reaction had subsided, the contents of the flask were heated for 24 hr at 93°. Distillation under reduced pressure afforded 27.48 g (75.5% yield) of methyldichlorosilylpentenes, bp 60–63° (15 mm), n^{24}D 1.4191.

The methyldichlorosilylpentenes from the reaction above were added dropwise to 125 ml of 3 *M* methylmagnesium chloride. After the addition, the mixture was refluxed for 3 hr and cooled. The contents of the flask were poured into ice water, and ammonium chloride and hydrochloric acid were added until the ether and aqueous layers became clearly separable. The organic layer was separated from the aqueous layer, and this aqueous layer was extracted three times with ether. The organic phases were combined and dried over anhydrous sodium sulfate. The mixture was distilled under reduced pressure, yielding 14.10 g (66.2% yield) of trimethylsilylpentenes, bp 56° (43 mm). Analysis by glpc using column A gave the following product composition: **1**, 1-trimethylsilyl-4-pentene (87.2%); **2**, *cis*-1-trimethylsilyl-2-pentene (9.3%); and **5**, *cis*-1-trimethylsilyl-3-pentene (3.5%). Product **1** was separated on column B using preparative gas chromatography. The infrared spectrum of 1,1-trimethylsilyl-4-pentene showed peaks at 3095 (vinyl CH), 2950, 2870, (CH), 1645 (CC), 1460 (CH), 1440 (vinyl CH), 1420 ($SiCH_3$), 1255 ($SiCH_3$), 915 (vinyl CH), 850 (SiC), and 695 cm^{-1} (SiC).

Anal. Calcd for $C_8H_{18}Si$: C, 67.50; H, 12.77. Found: C, 67.50; H, 12.72.

Hydrogenation of the Trimethylsilylpentene Mixture.—A 12% solution by volume of trimethylsilylpentenes from the reaction above in 50 ml of ethyl acetate was hydrogenated over platinum oxide (0.1 g) at 40 psi initial pressure. The products and reactants were analyzed by glpc using column A. Two products were formed in a 97% yield. The first product was 2.3% of the mixture and had the same retention time as 2-pentyltrimethylsilane. The second (97.7%) corresponded to 1-pentyltrimethylsilane.

Addition of Methyldichlorosilane to *trans*-1,3-Pentadiene.—The reaction was identical with that described for 1,4-pentadiene, except that this reaction was not exothermic and had to be continually heated for 24 hr to achieve a solution temperature of 95°. Distillation yielded 27.27 g (74.6% yield) of methyldichlorosilylpentenes, bp 64–65° (23 mm).

The apparatus and general procedure for methylating the methyldichlorosilylpentenes were the same as described above. Methylmagnesium chloride (0.660 mol in 220 ml of ether solution) was used to react with 27.27 g (0.149 mol) of methyldichlorosilylpentenes. After hydrolysis, extraction, and drying over anhydrous sodium sulfate, the products were distilled, affording 11.22 g (53.1% yield) of trimethylsilylpentenes, bp 46–47° (43 mm).

The product mixture was injected into a gas chromatograph using column A as previously described. The presence of three products was shown: **3**, *trans*-2-trimethylsilyl-3-pentene (39.1%); **4**, *trans*-1-trimethylsilyl-2-pentene (18.9%); and **2**, *cis*-1-trimethylsilyl-2-pentene (42.0%). In addition, this product was injected into the capillary column C to give **2** (36.9%), **5** (5.1%), **3** (39.1%), and **4** (18.2%). Using preparative gas chromatography, products **2**, **3**, and **4** were separated on column B at 73°.

The following spectra of **3**, *trans*-2-trimethylsilyl-3-pentene, was obtained: ir (neat) 3050 (vinyl CH), 2990 (CH), 2900 (CH), 1675 (CH), 1470 (CH), 1395 ($SiCH_3$), 1265 ($SiCH_3$), 1005 (trans olefin), 860 (SiC), and 705 cm^{-1} (SiC); nmr τ 10.37 (s, 9), 9.28 (d, 3), 8.92 (m, 1), 8.68 (d, 3), 5.02 (m, 2).

Anal. Calcd for $C_8H_{18}Si$: C, 67.50; H, 12.77. Found: C, 67.58; H, 12.60.

Isolated **4**, *trans*-1-trimethylsilyl-2-pentene, n^{25}D 1.465, had the following infrared spectrum: 2900 (CH) 1650 (C=C), 1460 (CH), 1650 (C=C), 1460 (CH), 1400 ($SiCH_3$), 1250 ($SiCH_3$), 990 (trans olefin), and 850 cm^{-1} (SiC).

Anal. Calcd for $C_8H_{18}Si$: C, 67.50; H, 12.77. Found: C, 67.73; H, 12.85.

cis-1-Trimethylsilyl-2-pentene (**2**), n^{25}D 1.4259, had the following spectra: ir (neat) 3020 (CH), 2990 (CH), 2905 (CH), 1665 (C=C), 1470 (CH), 1425 (cis olefin), 1440 ($SiCH_3$), 1255 ($SiCH_3$), 860 (SiC), 705 (SiC), and 670 cm^{-1} (cis olefin); nmr τ 10.30 (s, 9), 9.35 (t, 3), 8.83 (d, 2), 8.27 (m, 2), and 5.00 (m, 2).

Anal. Calcd for $C_8H_{18}Si$: C, 67.50; H, 12.77. Found: C, 67.25; H, 12.52.

Hydrogenation of Trimethylsilylpentene Mixture.—The procedure was the same as that described for the hydrogenation of trimethylsilylpentenes from the 1,4-pentadiene addition, except that for complete hydrogenation to take place, 16 hr under a pressure of 40 psi was necessary. The reaction was followed by glpc using column A. The overall yield of products was 88% and the product composition was 37.4% 2-pentyltrimethylsilane and 62.6% 1-pentyltrimethylsilane.

Hydrogenation of *cis*-1-Trimethylsilyl-2-pentene.—A 12% solution of **2**, *cis*-1-trimethylsilyl-2-pentene, in 25 ml of ethyl acetate was hydrogenated separatedly over platinum oxide. The procedure was identical with that described above. Product **2** yielded 1-pentyltrimethylsilane exclusively. The yield was 99% as determined by glpc.

Addition of Methyldichlorosilane to *cis*-1,3-Pentadiene.—The reaction was identical with that of *trans*-1,3-pentadiene. Distillation gave 29.55 g (82.2% yield) of methyldichlorosilylpentenes, bp 75–76° (43 mm).

The methylation procedure was identical with that already described for the methyldichlorosilanes from *trans*-1,3-pentadiene, except that 29.55 g (0.161 mol) of methyldichlorosilylpentenes was used. The yield was 22.88 g (75.5%) of trimethylsilylpentenes, bp 52–56° (43 mm). Gas chromatography using column A showed the presence of five products: **3** (10.5%), **4** (4.2%), **1** (1.3%), **2** (23.2%), and **5** (60.8%). Using column C five peaks were also found: **3** (16.0%), **4** (4.1%), **1** (2.0%), **2** (1.3%), and **5** (76.6%). Preparative gas chromatography, using column B, was used to obtain **5**: ir (neat) 3070 (CH), 3010 (CH), 2950 (CH), 1660 (C=C), 1450 (CH), 1405 ($SiCH_3$), 1250 ($SiCH_3$) 850 (SiC), 695 (SiC), and 675 cm^{-1} (cis olefin); nmr (impure sample) τ 10.20 (s), 9.60 (m), 8.63 (d), 4.82 (m).

Anal. Calcd for $C_8H_{18}Si$: C, 67.50; H, 12.77. Found: C, 67.35; H, 12.60.

Hydrogenation of Trimethylsilylpentene Mixture.—This hydrogenation procedure was identical with the hydrogenation of the previous trimethylsilylpentene mixtures. By glpc using column A it was shown that hydrogenation proceeded to give a 97% yield of two products, 2-pentyltrimethylsilane (8.9%) and 1-pentyltrimethylsilane (91.1%).

Preparation of 1-Pentyltrimethylslane.—The procedure of Whitmore, *et al.*,[23] was followed by allowing 15.1 g (0.10 mol) of 1-bromopentane to react with 2.5 g (0.10 mol) of magnesium turnings in 100 ml of dry ether, and then adding 21.8 g (0.20 mol) of trimethylchlorosilane in 20 ml of dry ether. The dried ether layer was distilled to give 5.2 g (36%) of 1-pentyltrimethylsilane: bp 137–138°; n^{20}D 1.4096 (lit.[23] bp 139.3°; n^{25}D 1.4069); ir (neat) 2800 (CH), 1460 (CH), 1410 ($SiCH_3$), 1250 ($SiCH_3$), 850 (SiC), and 695 cm^{-1} (SiC); nmr τ 9.67 (m, 2), 9.25 (m, 3), and 8.85 (m, 6).

Preparation of 2- and 3-Pentyltrichlorosilane.—Using the procedure of Speier and Webster,[24] 37.6 g (74.2%) of 2- and 3-pentyltrichlorosilanes was prepared, bp 162–164° (lit. bp 165–168° [24]).

The 2- and 3-pentyltrichlorosilanes were methylated using 425 ml (1.275 mol) of 3 *M* methylmagnesium chloride. Distillation gave 5.71 g (22.7%) of 2- and 3-pentyltrimethylsilanes, bp 130–

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[23] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. Van Strein, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Amer. Chem. Soc.*, **68**, 475 (1946).

[24] J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

149°, n^{24}_{D} 1.4187. These products were separated by preparative glpc using column B at 73°.

The 2-pentyltrimethylsilane (54%) gave the following spectra: ir 2900 (CH), 1460 (CH), 1400 ($SiCH_3$), 1250 ($SiCH_3$), and 850 cm^{-1} (SiC); nmr τ 10.16 (s, 9), 9.25 (m, 7), 8.82 (m, 4).

Anal. Calcd for $C_8H_{20}Si$: C, 66.58; H, 14.00. Found: C, 66.81; H, 13.78.

1-Bromo-2-pentyne.—1-Hydroxy-2-pentyne[25] (21.74 g, 0.258 mol), 100 ml of dry ether, and 4.3 ml of pyridine were allowed to react with 33 g (0.12 mol) of phosphorus tribromide using a published procedure.[25] Distillation under reduced pressure afforded 21.99 g (78.3%) of 1-bromo-2-pentyne, bp 77–80° (60 mm) [lit.[25] bp 147–148° (754 mm)].

1-Trimethylsilyl-2-pentyne.—1-Bromo-2-pentyne (10 g, 0.068 mol) in 25 ml of dry ether was added slowly to a mixture of 1.65 g (0.068 mol) of magnesium and 10 g (0.092 mol) of trimethylchlorosilane in 25 ml of dry ether. After refluxing for 3 hr, the reaction mixture was hydrolyzed and the ether layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 0.95 g (14%) of 1-trimethylsilyl-2-pentyne.

The following spectra were obtained: ir (neat) 2960 and 2890 (CH), 220 ($C{\equiv}C$), 1455 (CH), 1400 ($SiCH_3$), 1250 ($SiCH_3$), 850 (SiC), and 695 cm^{-1} (SiC); nmr τ 10.21 (s, 9), 9.30 (t, 3), 9.00 (t, 2), 8.28 (m, 2).

***cis*- and *trans*-Trimethylsilyl-2-pentene.**—The trimethylsilylpentyne prepared above was dissolved in 25 ml of ethyl acetate and hydrogenated over platinum oxide at 20 psi initial pressure. Analysis by glpc on column A at 73° showed 11% *trans*-1-trimethylsilyl-2-pentene and 76% *cis*-1-trimethylsilyl-2-pentene.

***cis*- and *trans*-3-Penten-1-ol.**—Hydrogenation of 31.2 g (0.363 mol) of 3-pentyne-1-ol in 75 ml of methanol over platinum oxide yielded 23.9 g (75%) of crude 3-penten-1-ol (9% trans and 82% cis by glpc), bp 141–142° (753 mm) [lit.[26] bp 129.9° (628 mm)].

***cis*- and *trans*-1-Bromo-3-pentene.**—Using the procedure cited above, 20.7 g (0.23 mol) of the 3-penten-1-ol mixture was converted into the corresponding 1-bromo-3-pentenes with 6.43 g of pyridine and 9.2 ml (0.097 mol) of phosphorous tribromide. There was obtained 21.54 g (60%) of the product, bp 129° (750 mm), n^{20}_{D} 1.4695 [lit.[26] bp 121.7° (621 mm), n^{20}_{D} 1.4695]. Preparative glpc with column B yielded 18% of *trans*-1-bromo-3-pentene, ir (neat) 3000 (CH), 1650 ($C{=}C$), 960 (trans CH), and 635 cm^{-1} (CBr), and 70.8% of *cis*-1-bromo-3-pentene, ir (neat) 2950 (CH), 1650 ($C{=}C$), and a broad band from 720 to 550 cm^{-1} attributed to cis C–H bending and C–Br stretch.

***cis*- and *trans*-1-Trimethylsilyl-3-pentene.**—By the method described above for 1-trimethylsilyl-2-pentyne, 5.0 g (0.034 mol) of the 1-bromo-3-pentene mixture was converted into 1.46 g (30.7% yield) of 1-trimethylsilyl-3-pentenes, bp 68–72° (101 mm) [lit.[27] bp 139.8 (756.5 mm)]. The product, analyzed by glpc using column A, consisted of a trace of 1-trimethylsilylpentane, *trans*-1-trimethylsilyl-3-pentene (20%), and *cis*-1-trimethylsilyl-3-pentene (79%).

1-Trimethylsilyl-4-pentene.—The procedure described by Benkeser, Smith, and Noe[18] was followed to yield 3.19 g of product (33.6% yield).

***cis*- and *trans*-1-Trimethylsilylpentenes.**—These were prepared *via* the peroxide-catalyzed addition of trichlorosilane to 1-pentyne as described by Benkeser, *et al.*[11]

Addition of Methyldichlorosilane to 2-Pentyne.—2-Pentyne (10.0 g, 0.148 mol) and 10.9 g (0.148 mol) of methyldichlorosilane were allowed to react in cyclohexane as described previously for the pentadiene additions. There was obtained 10.71 g (39.6%) of methyldichlorosilylpentenes, bp 55–58° (90 mm).

Methylation with 3.2 *M* methylmagnesium chloride (0.16 mol) afforded 6.17 g (74.2%) of trimethylsilylpentenes, bp 71–73° (91 mm). The 2- and 3-trimethylsilyl-2-pentenes produced showed different glpc retention times than any of the pentadiene addition products.

Addition of Methyldichlorosilane to Excess Pentadienes in the Presence of a Chloroplatinic Acid Catalyst.—In a typical procedure, to a 100-ml three-necked flask equipped with an addition funnel, a thermometer (in the solution), and a Dry Ice–acetone condenser were added 10 ml (0.095 mol) of methyldichlorosilane, 15 ml (0.15 mol) of *trans*-1,3-pentadiene, 25 ml of cyclohexane, and three drops of 0.2 *M* chloroplatinic acid. The isomeric purity of the pentadiene was checked initially and after refluxing at 58° for 24 hr using glpc with column A at 25°. Before refluxing only *trans*-1,3-pentadiene was detected. After 24 hr of refluxing, the composition was again checked for the unreacted pentadiene. The mixture was then distilled under reduced pressure to give the methyldichlorosilylpentenes. See Table II.

Competition Reaction between *cis*- and *trans*-1,3-Pentadienes.—To a pressure flask 25 ml of cyclohexane, 2 drops of 0.2 *M* chloroplatinic acid, 10 ml (0.10 mol) of methyldichlorosilane, 6.8 g (0.1 mol) of *cis*-1,3-pentadiene, and 6.8 g (0.1 mol) of *trans*-1,3-pentadiene were added. The flask was sealed and heated at 91° for 24 hr. After cooling, the mixture was injected into the gas chromatograph using column A at 25°. Three peaks resulted. The one with the longest retention time was cyclohexane; the first or the one with the shortest retention time was *trans*-1,3-pentadiene (27.6 area %); the remaining peak was *cis*-1,3-pentadiene (72.4 area %). This same mixture was injected into a 0.5-in. diameter, 19-ft column (15% SE-30 on 30–60 mesh firebrick) at 110°. Three additional components were detected; the first was 38.2 area %, the second was 35.4 area %, and the last was 26.4 area % of the mixture of methyldichlorosilylpentenes. Vacuum distillation yielded 14.93 g (40.7%) of methyldichlorosilylpentene, bp 62–64° (14 mm).

The products were methylated using 75 ml (0.225 mol) of 3 *M* methylmagnesium chloride. Distillation afforded 8.83 g (75.9% yield) of products, bp 57–59° (41 mm). Four peaks resulted from glpc analysis and were identified as **3**, *trans*-2-trimethylsilyl-3-pentene (35.3%), **4**, *trans*-1-trimethylsilyl-2-pentene (1.9%), **2**, *cis*-1-trimethylsilyl-2-pentene (39.3%), and **5**, *cis*-1-trimethylsilyl-3-pentene (23.5%), by their retention times.

Registry No.—**1**, 763-21-3; **2**, 40762-94-5; **3**, 40762-95-6; **4**, 40795-28-6; **5**, 40762-96-7; methyldichlorosilane, 75-54-7; 1-pentyltrimethylsilane, 1641-49-2; 3-pentyltrimethylsilane, 40748-37-6; 2-pentyltrimethylsilane, 40748-38-7; 1-trimethylsilyl-2-pentyne, 40748-39-8; 1-bromo-2-pentyne, 16400-32-1.

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