where

k = rate constant (1. mole^{-1} sec.$^{-1}$)
A = concentration of amine (mole 1.$^{-1}$)
B = concentration of decaborane (mole 1.$^{-1}$)
a = initial number of moles of amine in reaction
b = initial number of moles of decaborane in reaction
x = moles of hydrogen evolved in time, t

The reactions of decaborane with p-toluidine, p-anisidine, p-chloroaniline and aniline were run at 20.0°, 25.0°, 30.3° and 35.9°. From the rate constants obtained for these reactions the activation energies were calculated. Rate constants were also calculated for the reaction of decaborane with N-methylaniline and N,N-dimethylaniline in benzene solution at 25°.

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part VI. Addition to Branched Olefins
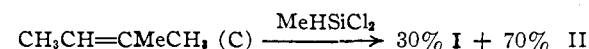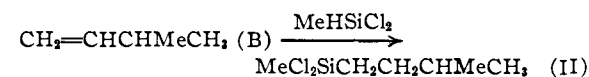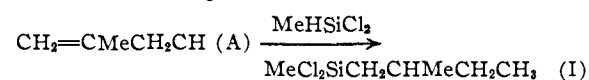
BY JOHN SAAM AND JOHN SPEIER

After the addition of methyldichlorosilane to an excess of an olefin in the presence of chloroplatinic acid, the excess olefin is recovered as a mixture of isomers. The process was studied with each of the methylbutenes, 1- and 4-methylcyclohexene and methylenecyclohexane. The distribution of the isomeric adducts obtainable under various conditions and the factors involved in the formation of isomeric olefins were studied.

Normal alkylsilanes result from the addition of silicon hydrides to linear olefins in the presence of chloroplatinic acid. This was found to be true even with non-terminal olefins. Pentene-2[1] gave n-pentylsilanes, and heptene-3[2] gave n-heptylsilanes. In these examples the silicon atom became attached exclusively to the terminal position on the alkyl chain.

To extend these observations, a study was undertaken to determine the positions favored by silicon during the addition of methyldichlorosilane to the methylbutenes in which there are distinguishably different terminal positions and to methylenecyclohexene and to 1- and 4-methylcyclohexenes in which there is only one terminal position.

An excess of each olefin, methyldichlorosilane and chloroplatinic acid were heated together. In each case one or more adducts formed and the excess olefin was recovered as a mixture of isomers.

The methylbutenes formed good yields of adducts outlined in the equations

$$CH_2=CMeCH_2CH \text{ (A)} \xrightarrow{\text{MeHSiCl}_2} MeCl_2SiCH_2CHMeCH_2CH_3 \text{ (I)}$$

$$CH_2=CHCHMeCH_3 \text{ (B)} \xrightarrow{\text{MeHSiCl}_2} MeCl_2SiCH_2CH_2CHMeCH_3 \text{ (II)}$$

$$CH_3CH=CMeCH_3 \text{ (C)} \xrightarrow{\text{MeHSiCl}_2} 30\% \text{ I} + 70\% \text{ II}$$

The adducts I and II were treated with methylmagnesium bromide to make the corresponding (methylbutyl)-trimethylsilanes. Authentic samples of these were synthesized as standards so that the identity of I and II could be established and their purity estimated by gas chromatography. In this way I and II were found to be quite pure. No trace of one was to be found in the other despite the fact that the olefins A and B were largely recovered as C. The purity of I and II seemed to require that either C was not made from A and B while the bulk of I and II were forming or else C was so unreactive that even if it were present

it did not compete detectably in forming adducts in the presence of A or B.

One equivalent of A and one equivalent of B were made to compete for one equivalent of methyldichlorosilane. The same was done with A and C, and with A and methallyl chloride. The products were analyzed by gas chromatography and the relative reactivities of the olefins were then calculated to be B/methallyl chloride/A/C = 1/0.8/0.07/0.02.

Branching as in A impedes the reaction, but a negative substituent accelerates the reaction. The rates of addition of both A and C differ only by a factor of about 3. The formation of essentially pure I from A cannot, therefore, be ascribed to the inability of C to compete with A, but indicates that C forms from A only after all or almost all of the I has been made.

Two experiments were run with an excess of methyldichlorosilane and A. In one case the two were mixed and sealed into a glass tube with the catalyst. A quantitative yield of pure I resulted. In the second case, the methyldichlorosilane was added slowly during three hours to the olefin at reflux. Again a quantitative yield was obtained, but the adduct was a mixture of 82% I with 18% II.

Methylenecyclohexane (D) gave an excellent yield of (cyclohexylmethyl)-methyldichlorosilane (III) free of isomers, but excess olefin was largely converted to 1-methylcyclohexene (E). 1-Methyl-

cyclohexene (E) or 4-methylcyclohexene (F) each formed both III and IV and excess olefin was re-
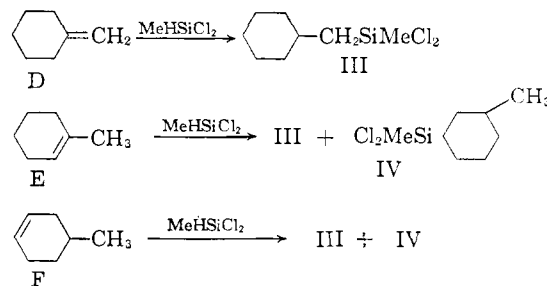
(1) J. L. Speier, J. A. Webster and G. H. Barnes, J. Am. Chem. Soc., 79, 974 (1957).

(2) J. C. Saam and J. L. Speier, ibid., 80, 4104 (1958).

covered largely in the form of E along with F. No 2- or 4-methylcyclohexylsilanes nor any 3-methylcyclohexene was detected during these experiments.

Trichlorosilane and F with acetyl peroxide as a free radical initiator gave mostly 4-methylcyclohexyltrichlorosilane with some of the 3-isomer.

Efforts were made to determine conditions in the mixtures that gave rise to the formation of isomers from the olefins. 2-Methylbutene-1 was heated with chloroplatinic acid alone and with methyl-dichlorosilane. Neither of these caused isomerization. A noticeable amount of isomers formed from the same olefin added to the non-volatile components of the reaction between pentene-1 and methyldichlorosilane. This mixture was likely to contain the active catalytic species that gives rise to the addition reaction. Somewhat more isomerization was obtained with pentene-1. Excess hexene-1 with methyldichlorosilane formed the hexylsilane in the presence of chloroplatinic acid. To the mixture pentene-1 was added after the reaction seemed complete. Pentene-2 was later identified in the mixture, although no pentylsilanes were detected.

These experiments suggest that an active catalytic species forms by a reaction of chloroplatinic acid and the silicon hydride. Perhaps an olefin also has a role in forming the active catalyst. The catalyst apparently exists after the addition reaction, by any usual standards, is complete. No stoichiometric relationships can be seen among the catalyst, silane and isomerized olefins.

The data can be rationalized by use of a scheme approximately represented as

$$\equiv SiH,\ Pt,\ O_1 \longrightarrow C_1^- \rightleftarrows C_2^- \rightleftarrows \text{etc.}$$
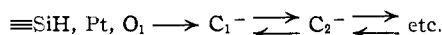
The process is thought of as beginning with a reaction between a silane, the platinum catalyst and the olefin resulting in the transfer of a hydride ion by nucleophilic attack upon a molecule of olefin, O_1, to give rise to a carbanion, C_1^-. The carbanion is thought of as capable of rapid tautomerization. The most stable carbanions would predominate in the mixture of tautomers and, therefore, terminal carbanions would likely be most available for the second step of the mechanism.

$$\equiv SiH + C_1^- + O_1 \longrightarrow \equiv SiR_1 + C_1^-$$
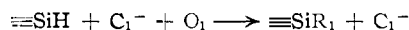
This step is visualized as nucleophilic attack of the carbanion upon a silane, perhaps to form a pentacovalent intermediate, $[\equiv SiRH]^-$, which in turn attacks a molecule of olefin to generate a new carbanion and a molecule of alkylsilane.

A third process may be thought of as responsible for the isomerization of the olefin

$$C_2^- + O_1 \rightleftarrows C_1^- + O_2$$
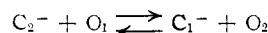
This step is thought to involve the transfer of a hydride ion from a carbanion to a molecule of olefin to generate a new molecule of olefin and a new carbanion. If C_1^- is a terminal carbanion and O_2 is a non-terminal olefin, the equilibrium should be far to the right.

In this way a plausible explanation can be given for the apparently exclusive formation of terminal alkylsilanes from non-terminal olefins such as

pentene-2, heptene-3, the methylcyclohexenes and 2-methylbutene-2. Stabilization by resonance of carbanions such as $CH_3CHC_6H_5$ explains why 1-phenylethylsilanes result from addition to styrene.[3]

The high degree of reactivity of methallyl chloride is thought of as due to the effect an electronegative substituent should have upon an olefin subjected to nucleophilic attack.

If a molecule of olefin is in a catalytically active platinum complex, the isomerizations may be a reversal of the first step of the reaction. All of these reactions may be taking place in a platinum–silane–olefin complex. Some of them might only originate in such a complex and propagate as a chain reaction throughout the medium. This would help explain how certain reactions could be extremely fast in the presence of 10^{-8} mole of catalyst per mole of reagents.[1]

In the near absence of silane toward the end of a reaction in excess olefin or during dropwise addition of silane to an olefin, the tautomerizations and transfer equilibria become the chief ones still taking place. These reactions could continue so long as the catalyst was still in an active form.

Experimental

Gas–liquid chromatography was carried out in a 10 ft. $\times\ 1/4''$ 304 stainless steel column packed with 28.6% DC-F-4050 on Chromosorb-R at 140° with a flow rate of 40 ml. of helium per minute.

Starting Materials. —The 2-methylbutene-1,3-methylbutene-1 and 2-methylbutene-2 were purchased from the Special Products Division of the Phillips Petroleum Co. and used without further purification. The 4-methylcyclohexene was purchased from Distillation Products Industries and redistilled; b.p. 102.5° (atm.), n^{25}D 1.4390; lit.[4] b.p. 102–103°, n^{20}D 1.4418. The 1-methylcyclohexene was prepared by the procedure of Mosher[5]; b.p. 109.5°, n^{25}D 1.4479, d^{25}_4 0.8065; lit.[6] b.p. 110° (atm.), n^{25}D 1.4477, d^{20}_4 0.8127. Methylenecyclohexane was prepared by the pyrolysis of cyclohexylmethyl acetate[7] in 57% yield; b.p. 102.5–103° (atm.), n^{25}D 1.4470; lit.[6] b.p. 100–102°, n^{25}D 1.4484. Gas–liquid chromatography showed that the product was pure and the infrared spectrum indicated that it was a terminal olefin. A 5% yield of 1-methylcyclohexene was also isolated.

Cyclohexylmethyl chloride was prepared by the usual procedure[8] from cyclohexylmethanol and thionyl chloride in chloroform solution; b.p. 164.5–165° (atm.), n^{25}D 1.4611, d^{25}_4 0.9755, RD 0.2816, calcd. RD 0.2821; lit.[9] b.p. 166°. In a similar manner 2-methylbutyl chloride was prepared from 2-methylbutanol; b.p. 98°, n^{55}D 1.4102, d^{25} 0.8806; lit.[10] b.p. 98–99° (atm.), n^{25}D 1.4101, d^{25}_4 0.8810. The 3-methylbutyl bromide was purchased from the Eastman Kodak Co. and was used without further purification.

o-, m- and p-tolyltrimethylsilanes were prepared by known procedures and the physical properties agreed with the previously reported values.[11]

Preparation of Standards. 2-Methylbutyltrimethylsilane was prepared from trimethylchlorosilane and 2-methyl-

(3) J. W. Ryan and J. L. Speier, J. Org. Chem., 24, 2052 (1959).

(4) R. T. Arnold, G. G. Smith and R. M. Dodson, ibid., 15, 1256 (1950).

(5) W. A. Mosher, J. Am. Chem. Soc., 62, 552 (1940).

(6) A. I. Vogel, J. Chem. Soc., 1323 (1938).

(7) W. J. Bailey, J. J. Hewitt and C. King, J. Am. Chem. Soc., 77, 357 (1955).

(8) W. R. Kirner and W. Windus, "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 136.

(9) P. Sabatier and A. Mailhe, Ann. chim. phys., 8, 10, 527 (1908).

(10) D. H. Brauns, J. Research Natl. Bur. Standards, 18, 323 (1937).

(11) (a) H. Frieser, M. Eagle and J. L. Speier, J. Am. Chem. Soc., 75, 2821 (1953); (b) H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, ibid., 73, 3798 (1951); (c) H. Soffer and T. DeVries, ibid., 73, 5817 (1951).

butyllithium; b.p. 133.5° (atm.), n^{25}D 1.4097, d^{25}_4 0.7335, RD 0.3376, calcd. RD 0.3388; lit.[12] b.p. 133–134°, n^{20}D 1.4064, d^{20}_4 0.7295.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 19.42.

3-Methylbutyltrimethylsilane was prepared from trimethylchlorosilane and 3-methylbutylmagnesium bromide, b.p. 128.0–129° (atm.), n^{25}D 1.4052, d^{25}_4 0.7247, RD 0.3384; calcd. RD 0.3388; lit.[13] b.p. 133–134° at 751 mm., n^{20}D 1.4064, d^{20}_4 0.7295.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 1954.

Cyclohexylmethyltrimethylsilane was prepared in ether from cyclohexylmethyllithium made from 8.6 g. of lithium and 66.2 g. of cyclohexylmethyl chloride. An aliquot of this reagent was carbonated to cyclohexylacetic acid whose amide melted at 166–169°, lit.[14] m.p. 167.5–168.6°. To this reagent was added 54.2 g. of trimethylchlorosilane to give 27.3 g. of cyclohexylmethyltrimethylsilane, b.p. 187–188°, n^{25}D 1.4455, d^{25}_4 0.8113, RD 0.3284, calcd. RD 0.3288. A gas–liquid chromatogram indicated no impurities.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.48.

2-Methylcyclohexyltrimethylsilane was prepared by reducing 82 g. of o-tolyltrimethylsilane with 3 g. of Raney nickel and 1100 p.s.i. of hydrogen at 100° in a 1.4-liter rocking bomb. The solvent was 300 ml. of methylcyclohexane. The hydrogen absorption was complete in 30 minutes. After washing with concentrated sulfuric acid and water, the mixture was distilled and gave 40 g. of 2-methylcyclohexyltrimethylsilane, b.p. 188–188.5°, n^{25}D 1.4560, d^{25}_4 0.8315, RD 0.3270, calcd. RD 0.3288. A gas–liquid chromatogram indicated that the product was pure.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.60.

3-Methylcyclohexyltrimethylsilane was prepared in the same manner as the 2-isomer except that the reduction, carried out with 76.5 g. of m-tolyltrimethylsilane, required 2.5 hours at 150° at 1700 p.s.i. of hydrogen for complete adsorption of hydrogen. Distillation gave 50 g. of 3-methylcyclohexyltrimethylsilane, b.p. 148–185°, n^{25}D 1.4475, d^{25}_4 0.8132, RD 0.3284, calcd. RD 0.3288. A gas–liquid chromatogram indicated that the product was pure.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.63.

4-Methylcyclohexyltrimethylsilane was prepared by reducing 82.5 g. of p-tolyltrimethylsilane in the same manner as the other isomers. The reduction was difficult to carry to completion at 165° and 2400 p.s.i. of hydrogen. Distillation gave 27 g. of 4-methylcyclohexyltrimethylsilane, b.p. 188.5°, n^{25}D 1.4520, d^{25}_4 0.8205, RD 0.3288, calcd. RD 0.3288.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.57.

A gas–liquid chromatogram indicated that the product contained 27 mole per cent. of the starting material.

Known mixtures were prepared from these standards and separated effectively by gas chromatography. Although cis-trans isomers might be expected among the three (methylcyclohexyl)-trimethylsilanes, each seemed to be a pure species and not a mixture. Cyclohexylmethyltrimethylsilane and 4-methylcyclohexyltrimethylsilane made up the only pair which could not be separated by gas chromatography. Fortunately the physical properties of the two are sufficient to distinguish them, and their H^1 n.m.r. spectra are characteristic.

Addition Reactions. Methyldichlorosilane and 3-Methylbutene-1.—3-Methylbutene-1 (31 g., 0.44 mole), methyldichlorosilane (57.5 g., 0.5 mole) and 0.1 ml. of 0.02 M chloroplatinic acid in alcohol were sealed in a Carius tube at Dry Ice temperature. An exothermic reaction took place when the tube approached room temperature. The mixture was carefully fractionated into two fractions. The first, b.p. 45–60°, 12.0 g., was, according to gas–liquid chromatography, 0.7% 3-methylbutene-1, 47.3% 2-methylbutene-2, 2.1% 2-methylbutene-1, 1.1% methyltrichlorosilane and 48.8% of methyldichlorosilane. The second

(12) A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk., S.S.S.R., Oidel. Khim. Nauk.*, 635 (1952); *C. A.*, **48**, 4462g (1954).

(13) A. V. Topchiev, N. S. Nametkin and T. I. Chernysheva, *Proc. Akad. Sci. USSR*, **115**, 326 (1957).

(14) M. Newman and C. A. VanderWerf, *J. Am. Chem. Soc.*, **67**, 236 (1945).

fraction was 75.0 g., 0.41 mole, 93% yield of 3-methylbutylmethyldichlorosilane, b.p. 163.5°, n^{25}D 1.4312, d^{25} 0.9958, RD 0.2599, calcd. RD 0.2590.

Anal. Calcd. for $C_6H_{14}Cl_2Si$: Si, 15.18; neut. equiv., 92.5. Found: Si, 15.23; neut. equiv., 95.5.

With 500 ml. of methylmagnesium bromide in ether prepared from 20.3 g. of magnesium, 50.5 g. of the above adduct was converted to 23.8 g. of 3-methylbutyltrimethylsilane, b.p. 128°, n^{25}D 1.4052, d^{25} 0.7236, RD 0.3389, calcd. RD 0.3388. A gas–liquid chromatogram indicated that the product was pure and indistinguishable from an authentic sample.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 19.52.

Methyldichlorosilane and 2-Methylbutene-1.—To 70 g. (1 mole) of 2-methylbutene-1 and 0.1 ml. of 0.02 M chloroplatinic acid in ethanol was added a 10-ml. portion of 57.5 g. (0.5 mole) of methyldichlorosilane. After the exothermic reaction subsided, the remaining methyldichlorosilane was added at a rate that would maintain reflux. The mixture was separated into two fractions by distillation. The first fraction, 35.0 g., b.p. 38–45°, was 67.9% 2-methylbutene-1 and 31.6% 2-methylbutene-2 according to gas–liquid chromatography. The second fraction was 82.5 g., 0.45 mole, 90% yield, of 2-methylbutylmethyldichlorosilane, b.p. 167°, n^{25}D 1.4357, d^{25} 1.007, RD 0.2595, calcd. RD 0 2590.

Anal. Calcd. for $C_6H_{14}Cl_2Si$: Si, 15.18; neut. equiv., 92.5. Found: Si, 15.21; neut. equiv., 93.5.

Seventy grams of the 2-methylbutylmethyldichlorosilane with methylmagnesium bromide prepared from 24.3 g. of magnesium in 600 ml. of ether gave 40.1 g. of 2-methylbutyltrimethylsilane, b.p. 134°, n^{25}D 1.4095, d^{25} 0.7343, RD 0.3370, calcd. RD 0.3388. Gas–liquid chromatography revealed that the product was indistinguishable from an authentic sample.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 19.25.

Methyldichlorosilane (22.8 g., 0.198 mole), 2-methylbutene-1 (6.8 g., 0.98 mole) and 0.1 ml. of 0.1 M chloroplatinic acid in ethanol treated in the same way gave a quantitative yield of 2-methylbutyldichlorosilane free of detectable amounts of isomers.

Methyldichlorosilane (126.5 g., 1.1 moles) was added dropwise during 3 hours to a refluxing mixture of 2-methylbutene-1 (70.1 g., 1 mole) and 0.1 ml. of 0.1 N chloroplatinic acid. By this method, 179.8 g., 97%, of adduct was obtained, b.p. 164°, n^{25}D 1.4351, d^{25}_4 1.005. This adduct was methylated and found by gas chromatography to be 82% 2-methylbutyltrimethylsilane and 18% 3-methylbutyltrimethylsilane.

Methyldichlorosilane and 2-Methylbutene-2.—A mixture of 2-methylbutene-2 (70 g., 1 mole), methyldichlorosilane (57.5 g., 0.5 mole) and 0.1 ml. of 0.2 M chloroplatinic acid in ethanol was sealed in a tube at Dry Ice temperature and then heated on a steam-bath for 16 hours. Two fractions were separated by distillation. The first fraction, 35.7 g., b.p. 40–55°, was 93.2% 2-methylbutene-2, 5.5% 2-methylbutene-1 and 1.3% 3-methylbutene-1 according to gas–liquid chromatography. The second fraction was 87.2 g., 94.5% yield, of a mixture of I and II, b.p. 162–168°, n^{25}D 1.4322, d^{25} 0.9978, RD 0.2600, calcd. RD 0.2590.

Anal. Calcd. for $C_6H_{14}Cl_2Si$: Si, 15.18; neut. equiv., 92.5. Found: Si, 15.44; neut. equiv., 94.0.

With 500 ml. of methylmagnesium bromide in ether prepared from 24.3 g. of magnesium, 69.3 g. of the above mixture was converted to 35.5 g. of a mixture of 2-methylbutyltrimethylsilane and 3-methylbutyltrimethylsilane, b.p. 124–132°, n^{25}D 1.4060–1.4080, d^{25} 0.7301–0.7327, RD 0.3378–0.3367, calcd. RD 0.3388. By comparing a gas–liquid chromatograph of the above mixture with a mixture of authentic samples, it was found that the mixture was 31.1% 2-methylbutyltrimethylsilane and 68.9% 3-methyltrimethylsilane.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 19.35.

Methyldichlorosilane and Methylenecyclohexane.—Methyldichlorosilane (46 g., 0.4 mole) was added dropwise to methylenecyclohexane (48 g., 0.5 mole) containing 0.06 ml. of 0.33 M chloroplatinic acid. The rate of addition was regulated so that the temperature did not exceed 120°. The mixture was then distilled. Fraction 1 was

8.0 g. of a mixture made up of 13% methylenecyclohexane and 87% 1-methylcyclohexene according to gas–liquid chromatography; b.p. 101.5–110°. Fraction 2 was 81.2 g. (96%) of cyclohexylmethylmethyldichlorosilane, b.p. 136–136.5° at 65 mm., n^{25}D 1.4690, d^{45} 1.065, RD 0.2615, calcd. RD 0.2614.

Anal. Calcd. for $C_8H_{16}Cl_2Si$: Si, 13.29; neut. equiv., 105.5. Found: Si, 13.57; neut. equiv., 105.5.

Seventy-one grams of the above product was treated with 1 mole of methylmagnesium bromide in 600 ml. of ether in the usual manner and 48.7 g. (86%) of cyclohexylmethyltrimethylsilane was obtained, b.p. 189.5°, n^{25}D 1.4460, d^{25} 0.811, RD 0.3288, calcd. RD 0.3288. A gas–liquid chromatogram and H[1] n.m.r. spectra indicated that the product was identical to the authentic sample.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.18.

Methyldichlorosilane and 1-Methylcyclohexene.—A mixture of 1-methylcyclohexene (96 g., 1 mole), methyldichlorosilane (138 g., 1.22 moles) and 0.05 ml. of 1.0 molar chloroplatinic acid in alcohol was refluxed 48 hours. At intermittent periods an additional 0.5 ml. of 0.1 molar chloroplatinic acid in alcohol was added to the refluxing mixture. The mixture was separated into 59.7 g. of methyldichlorosilane and 42.6 g. of a mixture of olefins, b.p. 100–107°, which was 93% 1-methylcyclohexene and 7% 4-methylcyclohexene according to gas–liquid chromatography. The final fraction was 88.4 g. of a mixture of 3-methylcyclohexylmethyldichlorosilane and cyclohexylmethylmethyldichlorosilane, b.p. 146–148° at 99 mm., n^{25}D 1.4680–1.4686, d^{25} 1.063–1.065, RD 0.2616, calcd. RD 0.2614.

Anal. Calcd. for $C_8H_{16}Cl_2Si$: Si, 13.29; neut. equiv., 105.5. Found: Si, 13.26; neut. equiv., 105.7.

A portion, 65.7 g., of the mixture of isomeric adducts was converted with excess methylmagnesium bromide to 45.5 g. of a mixture consisting of 84% cyclohexylmethyltrimethylsilane and 16% 3-methylcyclohexyltrimethylsilane, b.p. 183–187°, n^{25}D 1.4441–1.4454, d^{25} 0.8113–0.8120, RD 0.3290, calcd. RD 0.3288. The identity of these compounds was assigned by comparing gas–liquid chromatograms of the above mixture with those of mixtures of authentic samples and by similar comparisons of H[1] n.m.r. spectra.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.78.

Methyldichlorosilane and 4-Methylcyclohexene.—In a similar manner 4-methylcyclohexene (115 g., 1.18 moles), methyldichlorosilane (115 g., 1.0 mole) and 0.05 ml. of 1.0 M chloroplatinic acid were refluxed 24 hours. Distillation gave 58.0 g. of methyldichlorosilane, 66.1 g. of a mixture of olefins, b.p. 101–110°, composed of 74% 1-methylcyclohexene and 26% 4-methylcyclohexene according to gas–liquid chromatography, and finally 54.5 g. of a mixture of 3-methylcyclohexylmethyldichlorosilane and cyclohexylmethylmethyldichlorosilane, b.p. 211–213°, n^{25}D 1.4679, d^{25} 1.062, RD 0.2616, calcd. RD 0.2614.

Anal. Calcd. for $C_8H_{16}Cl_2Si$: Si, 13.29; neut. equiv., 105.5. Found: Si, 12.90; neut. equiv., 106.5.

Forty-two grams of the mixture of adducts was treated with excess methylmagnesium bromide and the product was isolated in the usual manner to give 20.3 g. of a mixture of cyclohexylmethylmethyldichlorosilane and 3-methylcyclohexyltrimethylsilane, b.p. 181–185°, n^{25}D 1.4452, d^{25} 0.8109, RD 0.3283, calcd. RD 0.3288.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.31.

Gas–liquid chromatography and an H[1] n.m.r. spectrum indicated that only cyclohexylmethyltrimethylsilane and 3-methylcyclohexyltrimethylsilane were present and that the mixture was identical with that obtained from the 1-methylcyclohexene.

4-Methylcyclohexyltrichlorosilane.—A mixture of 4-methylcyclohexene (96 g., 1 mole) and trichlorosilane (135.5 g., 1 mole) was heated at reflux with 1 g. of tin for 24 hours. During this period a solution of 12 g. of acetyl peroxide in 100 ml. of benzene was slowly added. The volatile components were distilled from the mixture and the product was distilled at reduced pressure without rectification to give 61.5 g. of 4-methylcyclohexyltrichlorosilane, b.p. 112–113° at 32 mm., n^{25}D 1.4765, d^{25} 1.192, RD 0.2371, calcd. RD 0.2365.

Anal. Calcd. for $C_7H_{13}Cl_3Si$: Si, 12.13; neut. equiv., 77.2. Found: Si, 12.03; neut. equiv., 77.8.

Fifty grams of this product was treated with excess methylmagnesium bromide and gave 28.3 g. of 4-methylcyclohexyltrimethylsilane, b.p. 187–188°, n^{25}D 1.4463, d^{25} 0.8171, RD 0.3265, calcd. RD 0.3288. A gas–liquid chromatogram and H[1] n.m.r. spectrum showed that the product consisted of essentially the 4-methylcyclohexyltrimethylsilane with a trace of the 3-isomer.

Anal. Calcd. for $C_{10}H_{22}Si$: Si, 16.47. Found: Si, 16.11.

Competitive Addition Reactions. 2-Methylbutene-1 and 3-Methylbutene-1 with Methyldichlorosilane.—Methyldichlorosilane (23 g., 0.2 mole), 2-methylbutene-1 (14 g., 0.20 mole), 3-methylbutene-1 (14 g., 0.20 mole), and 0.1 ml. of 0.1 M chloroplatinic acid in ethanol was sealed into a Carius tube at Dry Ice temperature and heated at 60° for 16 hours. The mixture was then added dropwise to a stirred solution of 0.5 M of methylmagnesium bromide in 200 ml. of ether. The mixture of isomeric methylbutyltrimethylsilanes was isolated by distillation and gave a 66% yield, b.p. 127–136°, n^{25}D 1.4048, d^{25} 0.7259, RD 0.3386, RD calcd. 0.3388.

Anal. Calcd. for $C_8H_{20}Si$: Si, 19.45. Found: Si, 19.55.

Gas–liquid chromatography revealed that the mixture was 87% 3-methylbutyltrimethylsilane and 13% 2-methylbutylsilane. The ratio of rates for $CH_2=C(CH_3)CH_2-CH_3/(CH_3)_2CHCH=CH_2$ was then calculated as 0.07.[15]

2-Methylbutene-1 and 2-Methylbutene-2 with Methyldichlorosilane.—In a similar manner methyldichlorosilane (23 g., 0.2 mole), 2-methylbutene-2 (14.0 g., 0.20 mole), 2-methylbutene-1 (14.0 g., 0.20 mole) and 0.1 ml. of 0.1 M chloroplatinic acid in ethanol was converted to the trimethylsilyl derivatives in 71% yield, b.p. 129–135°, 1.4080, d^{25} 0.7336, RD 0.3373, calcd. RD 0.3388.

Anal. Calcd. for $C_8H_{20}Si$: Si 19.45. Found: Si, 19.28.

Gas–liquid chromatography revealed that the mixture was 80% 2-methylbutyltrimethylsilane and 20% 3-methylbutyltrimethylsilane. Based on the results of the addition to 2-methylbutene-2, 29% of the latter product resulted from addition to 2-methylbutene-1. The ratio of the rates for $CH_2=C(CH_3)CH_2CH_3/(CH_3)_2C=CHCH_3$ was then calculated to be 3.6.

2-Methylbutene-1 (A), Methallyl Chloride and Methyldichlorosilane.—2-Methylbutene-1 (17.5 g., 0.25 mole), methallyl chloride (22.6 g., 0.25 mole), methyldichlorosilane (27.8 g., 0.25 mole) and 0.025 ml. of 0.1 M chloroplatinic acid in isopropyl alcohol were sealed into a glass tube at Dry Ice temperatures and heated to 100° for several hours. Distillation gave recovered methylbutenes (14.41 g., 0.206 mole, 82% of original charge), methallyl chloride (4.0 g., 0.045 mole, 18% of original charge), (methylbutyl)-methyldichlorosilanes (6.98 g., 0.038 mole, n^{25}D 1.4370, d^{25} 1.011, 15% yield based on silane), and (2-methyl-3-chloropropyl)-methyldichlorosilane (42.9 g., 0.21 mole, 84% yield). The ratio for the rates of reaction of methallyl chloride and 2-methylbutene-1 was calculated from the yields of adducts, *i.e.*, 84 and 15%, to be 11.

Isomerization of 3-Methylbutene-1.—In an effort to cause isomerization of an olefin under the conditions used in carrying out the addition reactions but apart from the reaction, the following experiments were made.

3-Methylbutylmethyldichlorosilane was mixed with 3-methylbutene-1 in a ratio of 1 to 5 with 8×10^{-4} mole of chloroplatinic acid in ethanol per mole of olefin. The mixture was heated at 140° for 2 hours, and analyzed by gas chromatography. No olefin but 3-methylbutene-1 was detected.

The same procedure was used with a mixture of methyldichlorosilane and 3-methylbutene-1 with the same result.

A mixture of methyldichlorosilane with a 12-fold excess of 3-methylbutene-1 with 3.2 moles of chloroplatinic acid per mole of olefin was similarly treated. The recovered olefin was 90.5% 3-methylbutene-1, 7.1% 2-methylbutene-2 and 2.4% 2-methylbutene-1. Slightly more than one equivalent of olefin isomerized for each equivalent of silane charged.

The experiment was repeated using a 40% excess of pentene-1 and 3×10^{-4} equiv. of chloroplatinic acid. The

(15) The method of calculating relative rates from these data was that of C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1969 (1931).

recovered pentenes were 70.7% pentene-1 and 29.3% pentene-2.

Hexene-1 (0.020 mole), methyldichlorosilane (0.0123 mole) and 3 × 10⁻⁶ mole of chloroplatinic acid were sealed into a glass tube. An exothermic reaction occurred at about room temperature. About 0.5 hour later the tube was chilled in Dry Ice and opened. Pentene-1 (0.043 mole) was added. The tube was resealed and heated to 140° for 2 hours. The gas chromatogram in this case showed that the pentenes were 6% pentene-2. No pentylsilanes were detected.

A similar experiment was carried out with pentene-1 instead of hexene-1 above. The tube was opened after the reaction and evacuated to remove as much as the volatile compounds as possible at room temperature. 3-Methylbutene-1 was added to the tube. After 2 hours at 140°, the 3-methylbutene-1 (97%) was recovered along with 2.2% 2-methylbutene-2 and 0.4% 2-methylbutene-1.

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, OHIO UNIVERSITY, ATHENS, OHIO]

The Kolbe Electrolysis as a Source of Free Radicals in Solution. III. Some Aspects of the Stereochemistry of the Electrode Process

BY WILLIAM B. SMITH AND HANS-GEORG GILDE

The electrolysis of a methanolic solution of potassium propionate in the presence of butadiene yields the *trans* isomer only of 4-octene. Replacement of the propionate by optically active 2-methylbutanoic acid gave a fraction containing a $C_{16}H_{30}$ hydrocarbon which was not optically active nor was the ozonolysis product, 3-methylpentanoic acid. The electrolysis of a methanolic solution of potassium acetate in the presence of cyclohexadiene was found to result in both *cis*- and *trans*-1,2- and 1,4-addition of methyl groups to the diene.

Previous reports from this Laboratory[1] have established that the free radicals produced during the Kolbe electrolysis of potassium acetate will readily add to dienes and will cause vinyl polymerization. Several items mentioned in these reports have led us to investigate further the stereochemistry of the electrode process.
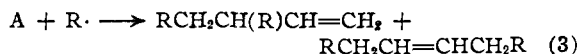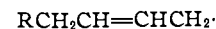
The first oddity noted was the fact that the electrolysis of a methanolic solution of potassium acetate in the presence of butadiene gave the *trans* isomer only of 3-hexene within the limits of infrared analysis and vapor phase chromatography (v.p.c.).[2] Replacement of the butadiene by isoprene led to the *cis* isomer only of 3-methyl-3-hexene. The polymerization of vinyl acetate during the electrolysis of potassium acetate produced a polymer which was unusually hard and brittle for its intrinsic viscosity. The polymer was shown to be neither isotactic nor highly cross linked suggesting, therefore, a high molecular weight linear structure.

In order to confirm the above data the electrolysis of potassium propionate in the presence of butadiene has now been carried out. The product work-up and examination was conducted as previously described.[1a] The infrared spectral examination of the appropriate hydrocarbon fractions gave evidence of the formation of the *trans* isomer only of 4-octene. No bands characteristic of the *cis* isomer could be found.

The formation of the unsaturated hydrocarbons during the electrolysis of a carboxylate in the presence of a diene radical acceptor has been previously pictured as

$$RCO_2^- \xrightarrow{-e} RCO_2 \cdot \longrightarrow R \cdot + CO_2 \quad (1)$$

$$R \cdot + CH_2{=}CHCH{=}CH_2 \longrightarrow RCH_2\overset{\cdot}{C}HCH{=}CH_2 \quad (2)$$
$$\updownarrow \qquad\qquad A$$
$$RCH_2CH{=}CHCH_2 \cdot$$

$$A + R \cdot \longrightarrow RCH_2CH(R)CH{=}CH_2 + RCH_2CH{=}CHCH_2R \quad (3)$$

Surprisingly, no reports of the stereochemistry of simple 1,4-radical addition to butadiene are given in the literature. The subject has received consideration in the polymerization of butadiene, however. The data have been reviewed by Walling.[3] Here it has been observed that at room temperature the *cis* structure comprises about 33% of the 1,4-addition polymer. Evidence is available to support the view that allylic radicals of the type A above maintain their steric integrity. Walling, Jacknow and Thaler[4] have reported that the allylic chlorination of *trans*-2-butene with *t*-butyl hypochlorite yields only *trans*-1-chloro-2-butene and none of the *cis* isomer, while *cis*-2-butene gives only the *cis* isomer of 1-chloro-2-butene.

In discussing the double bond character of the 2,3-carbon bond in butadiene, Pauling has stated that the *s-trans* conformation of the molecule is more stable than the *s-cis* form.[5] Pritchard and Sumner[6] have given the value of 4 kcal./mole for the energy of interconversion. In contrast, Nikitin and Yakovleva[7] have concluded on the basis of a

(1) For preceding papers in this series see W. B. Smith and H.-G. Gilde, (a) *J. Am. Chem. Soc.*, **81**, 5325 (1959); (b) **82**, 659 (1960).

(2) Subsequent to the work reported in ref. 1a a more specific search for *cis*-3-hexene was carried out with the aid of an authentic sample of this material. No positive evidence for its existence in the reaction was found by either infrared spectroscopy or by v.p.c. Use of the authentic sample established the limit of detectability of *cis*-3-hexene at something less than 5% of the hydrocarbon fraction.

(3) Cheves Walling, "Free Radicals in Solution," John Wiley and Sons, Inc. New York, N. Y., 1957, pp. 228–232.

(4) C. Walling, B. B. Jacknow and W. Thaler, Abstracts, 136th National Meeting, American Chemical Society, Atlantic City, N. J.

(5) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, pp. 290–292.

(6) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc. (London)*, **A235**, 136 (1956).

(7) V. N. Nikitin and T. V. Yakovleva, *Zhur. Fiz. Khim.*, **28**, 697 (1954).