[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

# Studies in Organosilicon Chemistry. XXXIX. The Addition of Silanes to Isoprene

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The addition of trichlorosilane, methyldichlorosilane, ethyldichlorosilane, trimethylsilane, benzyldichlorosilane, and dibenzylchlorosilane to isoprene has been studied. In the presence of chloroplatinic acid as a catalyst, each of these except trimethylsilane forms a 1,4-adduct in excellent yields, and by the alkylation of these adducts with alkylmagnesium halides, tetrasubstituted derivatives are formed. From a study of the infrared spectra and the results of ozonolysis, the structure of the first adduct, trimethyl derivative, is deduced as 1-(trimethylsilyl)-2-methylbutene-2. Benzoyl peroxide is a poor catalyst for this reaction.

The general reactions by which silanes containing the silicon-hydrogen linkage add to diolefines have already received considerable attention.[1-8]

Bailey and Pines[1a] investigated the addition of trichlorosilane to butadiene in the presence of platinized carbon at 160° and obtained the 1,4-adduct as the monomeric product, namely $CH_3$-$CH{=}CHCH_2SiCl_3$. This adduct was prepared and after two fractionations was passed through a gas chromatograph. It was found to consist of but one component. The presence of unsaturation was determined by its absorption of hydrogen over a palladium-charcoal catalyst. Approximately the theoretical amount of hydrogen was added.

Similarly, trichlorosilane has been found to add to isoprene in isopropyl alcohol and under the catalytic influence of chloroplatinic acid to form an adduct $C_5H_9SiCl_3$. The action of methylmagnesium chloride on $C_5H_9SiCl_3$ easily caused complete methylation to $C_5H_9Si(CH_3)_3$. Ozonolysis of the methylation product resulted in the formation of hexamethyldisiloxane, acetone, and ethyl acetate. The over-all series of reactions could be represented as follows:

$$CH_2{=}CHC(CH_3){=}CH_2 + SiHCl_3 \longrightarrow CH_3CH{=}C(CH_3)CH_2SiCl_3$$

$$CH_3CH{=}C(CH_3)CH_2SiCl_3 + 3CH_3MgCl \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(CH_3)_3 + 3MgCl_2$$

$$2CH_3CH{=}C(CH_3)CH_2Si(CH_3)_3 + 2\,O_3 + HOH \rightarrow 2CH_3CHO + 2CH_3COCH_3 + O_2 + (CH_3)3SiOSi(CH_3)_3$$

$$2CH_3CHO \longrightarrow CH_3COOC_2H_5.$$

The addition of other silanes to isoprene resulted in the formation of analogous isolable compounds. Reasoning by analogy, the formulas of these and their alkylation products, resulting from the action of methyl or ethyl Grignard reagents could be represented by the following:

$$CH_3SiHCl_2 \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(Cl)_2CH_3 \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(CH_3)_3$$

$$C_2H_5SiHCl_2 \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(Cl)2C_2H_5 \longrightarrow$$

see below, impure product, with slight test for SiH

$$C_6H_5CH_2SiHCl_2 \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(Cl)_2CH_2C_6H_5 \longrightarrow CH_2CH{=}C(CH_3)CH_2Si(C_2H_5)_2CH_2C_6H_5$$

$$(C_6H_5CH_2)_2SiHCl \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(CH_2C_6H_5)_2Cl \longrightarrow CH_3CH{=}C(CH_3)CH_2Si(CH_2C_6H_5)_2C_2H_5.$$

Trimethylsilane did not add to isoprene. 1-(Trimethylsilyl)-2-methylbutene-2 was cleaved to hexamethyldisiloxane by the action of sulfuric acid. The product resulting from the addition of ethyldichlorosilane to isoprene showed a slight positive test for silane hydrogen with caustic alkali.[9] A chlorine determination agreed qualitatively with the formula $C_5H_9Si(H)(Cl)C_2H_5$ or $C_5H_8$-$Si(H)(Cl)C_2H_5$. Therefore no statement should be made as to its structure.

A portion of the infrared spectrum of 1-(trimethylsilyl)-2-methylbutene-2 in the sodium chloride and lithium fluoride regions is given in Table II. Bands due to the trimethylsilyl group appear at 8.00, 11.64, 11.80, 13.26, and 14.43 μ. There is no evidence of the $C{=}CH_2$ at 3.26 where the other known isomer, 1-(trimethylsilyl)-3-methylbutene-3[10] has a prominent band. Bands due to CH, $CH_2$, and $CH_3$, are found at 3.37, 3.42, and 3.47 μ. $CH_2$ is found at 3.50 μ while other bands, due to stretching CH are found at 3.25, 3.27, and 3.30 μ. These are well known.[11] It will be seen from a

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[1a] D. L. Bailey and A. N. Pines, *Ind. Eng. Chem.*, 46, 2363 (1954).

[2] M. G. Voronkov and N. G. Romanova, *Zhur. Obshcheĭ Khim.*, 28, 2122 (1958).

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[4] D. B. Hatcher, U. S. Patent 2,665,287 (1954).

[5] G. H. Wagner, U. S. Patent 2,637,738 (1953).

[6] G. H. Wagner, U. S. Patent 2,632,013 (1953).

[7] L. A. Goldblatt and D. M. Oldroyd, U. S. Patent 2,750,462 (1950).

[8] A. J. Barry, Brit. Patent 671,747 (1952).

[9] J. W. Jenkins and H. W. Post, *J. Org. Chem.*, 15, 552 (1950).

[10] V. F. Mironov and N. A. Pogonkina, *Izvest. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk*, 182 (1955).

[11] *The Infrared Spectra of Complex Molecules*, L. J. Bellamy, London, 2nd ed., Chap. 2 (1958).

TABLE I

PHYSICAL PROPERTIES

| Compound | Yield, % | B.P. | Mm. | $n_D^{25}$ | $d_{25}^{25}$ |
|---|---|---|---|---|---|
| $CH_3CH{=}C(CH_3)CH_2SiCl_3$ | 60 | 161–162 | 760 | | 1.14[a] |
| | 76 | | | | |
| $CH_3CH{=}C(CH_3)CH_2Si(Cl)_2CH_3$ | 54 | 162–163 | 760 | | 1.03[a] |
| $CH_3CH{=}C(CH_3)CH_2SiHClC_2H_5$(?) | 27 | 172–178 | 760 | | 0.88[a] |
| $CH_3CH{=}C(CH_3)CH_2Si(CH_3)_3$ | 47 | 133–135 | 760 | 1.4256 | 0.7518 |
| | 68.2 | | | | |
| $CH_3CH{=}C(CH_3)CH_2Si(Cl)_2CH_2C_6H_5$ | 76 | 124–125 | 5 | 1.5429 | 1.0950 |
| $CH_3CH{=}C(CH_3)CH_2Si(C_2H_5)_2CH_2C_6H_5$ | 69 | 117 | 5 | 1.5114 | 0.8976 |
| $CH_3CH{=}C(CH_3)CH_2Si(CH_2C_6H_5)_2Cl$ | 42 | 153 | 2 | 1.5607 | 1.0489 |
| $CH_2CH{=}C(CH_3)CH_2Si(CH_2C_6H_5)_2C_2H_5$ | 43 | 147 | 2 | 1.5537 | 0.9723 |

[a] Unstable in air.

TABLE II

INFRARED DATA

| | $CH_3CH{=}C(CH_3)CH_2Si(CH_3)_3$ | $(CH_3)_2C{=}CHC_2H_5$ | $CH_3CH{=}C(CH_3)C_2H_5$[a] | |
|---|---|---|---|---|
| | | | *trans* | *cis* |
| CH stretching | 3.25, 3.27, 3.30 | None | 3.29 | 3.27, 3.30 |
| $CH_3$ | 3.37 | 3.37 | 3.37 | 3.37 |
| $CH_2$ stretching | 3.42 | 3.41 | 3.40 | 3.41, 3.42 |
| $CH_3$ | 3.47 | 3.47 | 3.47 | 3.47 |
| $CH_2$ | 3.50 | | 3.49 | |

[a] American Petroleum Institute, Infrared Spectral Data, No. 721 (*trans*), No. 720 (*cis*).

glance at Table II that this product has an infrared picture similar to that of the *cis* form of 3-methylpentene-2.

The infrared spectrum of the gas which was liberated by the action of sulfuric acid was taken in carbon tetrachloride solution and in a gas cell. Both spectra had the prominent absorption of 3.26 and 11.25 μ which are due to $RC{=}CH_2$. In addition, there was the absorption of hexamethyldisiloxane at 7.95, 9.45, 11.80, and 13.26 μ. Otherwise this spectrum was quite similar to that of 2-methylbutene-1 but not to that of 3-methylbutene-1 or of 2-methylbutene-2.[12] From the probability that the product was *cis* and was therefore stereospecifically prepared, it is reasonable to conclude that chloroplatinic acid acts as an ionic rather than as a free radical catalyst.

## EXPERIMENTAL

*General procedures.* A mixture of silane, isoprene, and catalyst was charged into a Pyrex glass Carius tube of 19-mm. diameter and about 150-cc. capacity which had been cooled in a Dry Ice–acetone bath, and the open end of the tube was fused after the air had been replaced by pure nitrogen. The reaction was carried out by heating in an electric furnace and the temperature was kept constant at 165° within 5°. After cooling, the tube was opened and the unchanged materials distilled. The remaining portion was distilled and fractionated.

*Trichlorosilane and isoprene.* A mixture of 136 g. (1.0 mole) of trichlorosilane and 68 g. (0.10 mole) of isoprene together with 3.1 × $10^{-5}$ mole of chloroplatinic acid in 0.1 mole of isopropyl alcohol was used, and heated for 17 hr. 1-(Trichlorosilyl)-2-methylbutene-2 was collected, b.p. 161–162°, $d_{25}^{25}$ 1.14, in 60% yield. A yield of 76% was obtained by the use of 1.5 moles of isoprene to 1.0 mole of trichlorosilane. A polymeric residue formed, upwards of 20% by weight.

*Anal.* Calcd. for $C_5H_9Cl_3Si$: Cl, 52.2. Found: Cl, 51.4.

*Methyldichlorosilane and isoprene.* Methyldichlorosilane (92 g., 0.8 mole) and isoprene (46 g., 0.67 mole) with 2.7 × $10^{-5}$ mole of chloroplatinic acid were allowed to react as described above. Practically all of the materials reacted, and 1-(methyldichlorosilyl)-2-methylbutene-2 was collected, b.p. 162–163°, $d_{25}^{25}$ 1.03, in 54% yield.

*Anal.* Calcd. for $C_6H_{11}Cl_2Si$: Cl, 38.8. Found: Cl, 38.4.

*Ethyldichlorosilane and isoprene.* A mixture of ethyldichlorosilane (54 g., 0.42 mole), isoprene (57 g., 0.84 mole) and chloroplatinic acid (2.8 × $10^{-5}$ mole) was allowed to react as previously described. Unchanged isoprene (5 g.) was recovered. The adduct distilled, b.p. 172–178° (760 mm.), $d_{25}^{25}$ 0.88. This product, 8.4 g., showed a positive test for silane hydrogen with caustic solution. Another fraction, 36.5 g., b.p. 179–184° was obtained, but its hydrolyzable chlorine content of 27.2% indicated considerable contamination.

*Anal.* Calcd. for $C_7H_{15}ClSi$: Cl, 21.6. Found: Cl, 20.6.

*1-(Trimethylsilyl)-2-methylbutene-2.* Methylmagnesium chloride solution, prepared from 16 g. (0.64 g.-atom) of magnesium turnings and methyl chloride, in tetrahydrofuran was dropped in 34 g. (0.167 mole) of 1-(trichlorosilyl)-2-methylbutene-2, with cooling. When cooling was no longer necessary, the mixture was refluxed for 30 min., then allowed to stand overnight. The upper layer was separated and the remaining solid portion hydrolyzed with aqueous saturated ammonium chloride solution. The upper layer and the ether extract of the lower layer were combined and distilled giving a main fraction, 1-(trimethylsilyl)-2-methylbutene-2, yield 68.2%, b.p. 133–135°, $n_D^{25}$ 1.4256, $d_{25}^{25}$ 0.7518.

*Anal.* Calcd. for $C_8H_{18}Si$: C, 67.51; H, 12.74. Found: C, 67.35; H, 12.55.

Similarly, the action of methylmagnesium chloride on 1-(methyldichlorosilyl)-2-methylbutene-2 also resulted in the formation of 1-(trimethylsilyl)-2-methylbutene-2.

*1-(Benzyldichlorosilyl)-2-methylbutene-2.* Benzyldichlorosilane was prepared according to the method given by

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[12] E. L. Purlee and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **78,** 5807 (1956).

Jenkins, Lavery, Guenther, and Post,[13] b.p. 67–68° (6 mm.), 51.2% yield. This compound (38.2 g., 0.2 mole), 20.7 g. (0.3 mole) of isoprene and $3.0 \times 10^{-5}$ mole of chloroplatinic acid in 0.1 mole of isopropyl alcohol were allowed to react as before, at 160° for 90 hr. No positive pressure was noticeable in opening the tube. Fractionation yielded 1-(benzyldichlorosilyl)-2-methylbutene-2, b.p. 124–125° (5 mm.), $n_D^{25}$ 1.5429, $d_{25}^{25}$ 1.0950, in 76.4% yield.

*Anal.* Calcd. for $C_{12}H_{16}Cl_2Si$: Cl, 27.36; Si, 10.82. Found: Cl, 27.04; Si, 10.84.

*1-(Benzyldiethylsilyl)-2-methylbutene-2.* Ethylmagnesium bromide, prepared from 8.5 g. of magnesium turnings in dry ethyl ether was added to 18.8 g. of 1-(benzyldichlorosilyl)-2-methylbutene-2 in dry ether at room temperature. Gentle reflux was induced for 60 hr. and the mixture hydrolyzed with a minimum amount of saturated ammonium chloride solution at 0°. Fractionation gave 1-(benzyldiethylsilyl)-2-methylbutane-2, b.p. 117° (5 mm.), $n_D^{25}$ 1.5114, $d_{25}^{25}$ 0.8976 in 68.9% yield.

*Anal.* Calcd. for $C_{16}H_{26}Si$: C, 77.97; H, 10.63; Si, 11.40. Found: C, 77.91; H, 10.41; Si, 11.30.

*1-(Dibenzylchlorosilyl)-2-methylbutene-2.* Dibenzylchlorosilane was prepared as was the monobenzyl compound[13] and treated with isoprene as was the above mentioned compound. 1-(Dibenzylchlorosilyl)-2-methylbutene-2 was isolated, b.p. 153° (2 mm.), $n_D^{25}$ 1.5607, $d_{25}^{25}$ 1.0489, in 42% yield.

*Anal.* Calcd. for $C_{14}H_{23}ClSi$: Cl, 11.26; Si, 8.92. Found: Cl, 11.22; Si, 8.89.

*1-(Ethyldibenzylsilyl)-2-methylbutene-2.* Ethylation was carried out as was the ethylation of the monobenzyl analog, giving 1-(ethyldibenzylsilyl)-2-methylbutene-2, b.p. 147° (2 mm.), $n_D^{25}$ 1.5537, $d_{25}^{25}$ 0.9723, in 43% yield.

*Anal.* Calcd. for $C_{21}H_{28}Si$: C, 81.75; H, 9.15; Si, 9.11. Found: C, 81.20; H, 9.11; Si, 9.23.

This compound and the three preceding, containing one or two benzyl groups, were indicated to be 96% pure by gas chromatography. Their infrared spectra also indicated that these compounds contained a 2-butene structure, showing 1,4-addition. The 3.40 μ stretching band was characteristic of all four products containing the benzyl group.

*Ozonolysis of 1-(trimethylsilyl)-2-methylbutene-2.* The silyl olefin (2.0 g.) was dissolved in 30 cc. of chloroform, dried over calcium chloride, and to this a stream of ozonized air was introduced for 2.5 hr. at 0°. The products in solution were investigated by gas chromatography (Kotaki Super Fractioner GU 21). Two 4-mm. inside diameter columns were used in this work: di-*n*-octyl phthalate on kieselguhr, 2 m., and tri-*m*-cresyl phosphate on kieselguhr, 1 m. Approximate operating conditions comprised, for the phthalate column 100°, 50 cc. of helium min., and for the phosphate column 75°, 40 cc. of helium min. For the phthalate column there was some overlapping of peaks but in most cases complete or nearly complete resolution was obtained. Hexamethyldisiloxane, acetone, and ethyl acetate peaks were detected in both columns. The presence of acetone was also confirmed by the formation of its 2,4-dinitrophenylhydrazone, m.p. 126–128°, after two recrystallizations, showing no depression when mixed with an authentic sample.

*Cleavage of 1-(trimethylsilyl)-2-methylbutene-2.* The sample (42 g.) was shaken with 80% sulfuric acid in a separatory funnel with intent to remove impurities. The evolution of a gas with an olefinic odor was noted and the color of the liquid acid phase turned dark brown. The liquid acid layer was removed to avoid further decomposition. On distillation, a fraction was obtained, b.p. 99°, $n_D^{24}$ which was identified as hexamethyldisiloxane and showed the marked absorption band of this compound at 9.45 μ.

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(13) J. E. Jenkins, N. L. Lavery, P. R. Guenther, and H. W. Post, *J. Org. Chem.*, **13**, 862 (1948).

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[CONTRIBUTION FROM WASHINGTON LABORATORY, RESEARCH AND DEVELOPMENT DIVISION, POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

# Reactions of Perfluorosultones with Ammonia[1]

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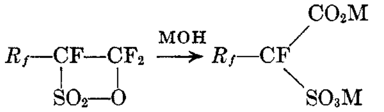
The reactions of perfluorosultones with ammonia lead to a variety of products depending upon the extent of ammoniation. A discussion of the chemistry of the ammoniation reactions and evidence for the determination of the new structures is presented.

Previous workers[2] have shown that perfluorosultones [3-perfluoroalkyl-3,4,4-trifluoro-1,2-oxathietane 2,2-dioxides, I] react with aqueous sodium or potassium hydroxide to produce the dialkali metal salt of the perfluoro-α-sulfocarboxylic acid II.



$$R_f\text{—}\underset{SO_2\text{—}O}{CF\text{—}CF_2} \xrightarrow{MOH} R_f\text{—}CF\begin{matrix}CO_2M\\SO_3M\end{matrix}$$

M = Na or K

Ia. $R_f = C_5F_{11}$ IIa. $R_f = C_5F_{11}$

b. $R_f = CF_3$ b. $R_f = CF_3$

The intermediate in this reaction is probably the α-fluorosulfonyl perfluoroalkanoyl fluoride III, as it has also been shown by the same authors that a trace of base such as triethylamine readily effected rearrangement of the sultone I to the diacid fluoride III. After bringing about a similar rearrangement,

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[1] Presented at the Fluorine Symposium sponsored by the Division of Industrial and Engineering Chemistry at the 138th meeting of the American Chemical Society, New York, N. Y.

[2] D. C. England, M. A. Dietrich, and R. V. Lindsey, *J. Am. Chem. Soc.*, **82**, 6181 (1960).