calculations, however, the constants directly determine from the compressibility data and presented in Table I should be used. It is to be remarked that the constants have compensating effect and that two sets of constants even with appreciable numerical differences may yield similar results so far as the compressibility, not the derivatives of the quantities, is concerned.

Acknowledgment.—The writers are grateful to Professor James A. Beattie and Professor Warren K. Lewis for their suggestions and encouragement.

Summary

1. A generalized form of Beattie–Bridgeman equation of state is proposed

$$\pi = \frac{\theta(1 - \epsilon)}{\varphi^2} [\varphi + B'] - \frac{A'}{\varphi^2}$$

where

$\epsilon' = c'/\varphi\theta^3$
$A' = A_0'(1 - a'/\varphi)$
$B' = B_0'(1 - b'/\varphi)$
$\pi = p/p$, reduced pressure
$\theta = T/T_c$, reduced temperature
$\varphi = V/V_{ci}$, ideal reduced volume
$V_{ci} = RT_c/p_c$, ideal critical volume

The constants A_0', a', B_0', b' and c' have the same numerical values irrespective of nature of gas as follows

$A_0' = 0.4758$ $B_0' = 0.18764$ $c' = 0.05$
$a' = 0.1127$ $b' = 0.03833$

2. The proposed generalized equation holds for seventeen gases with an average deviation of 2% or less for each gas up to nearly the critical density. It is believed that the proposed equation may be applied in general to all real gases.

RECEIVED JANUARY 31, 1946

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Organosilicon Compounds. V.[1] β-Eliminations Involving Silicon[2]

BY L. H. SOMMER, G. M. GOLDBERG, E. DORFMAN AND F. C. WHITMORE

α-Chloroethyltrichlorosilane with methylmagnesium bromide gives α-chloroethyltrimethylsilane with no attack on the alpha chlorine.[3]

$$CH_3CHClSiCl_3 + 3CH_3MgBr \longrightarrow CH_3CHClSi(CH_3)_3$$

In striking contrast, the corresponding beta chlorine is very reactive. Moreover it induces the splitting of the C–Si bond. β-Chloroethyltrichlorosilane with excess methylmagnesium bromide gives *tetramethylsilane* and *ethylene*. Similarly, ethylmagnesium bromide gave ethylene and tetraethylsilane. Stepwise addition of four equivalents of the Grignard reagent showed that the fission of the C–Si bond and the evolution of ethylene took place mainly as follows

$$ClCH_2CH_2Si(CH_3)_3 + CH_3MgBr \longrightarrow (CH_3)_4Si + CH_2{=}CH_2$$

In earlier work[1,3] we found the amazing reactivity of chlorine beta to silicon as shown by quantitative titration with 0.5 *N* alkali. We now report that this unusual activity is associated with fission of the C–Si bond to give the corresponding olefin. Thus an ether solution of β-chloroethyltrichlorosilane reacts vigorously at room temperature with aqueous alkali.

$$ClCH_2CH_2SiCl_3 \xrightarrow[H_2O]{OH^-} CH_2{=}CH_2 + Si(OH)_4 + 4Cl^-$$

In striking contrast is the action of the ether solution with water alone. Removal of the ether and heating at 170–180° for two hours leaves a clear brittle polymer in 80% yield. This polymer is β-chloroethyl silicone, $ClCH_2CH_2SiO_{1.5}$.[4] It reacts rapidly with dilute alkali to give ethylene.

$$ClCH_2CH_2SiO_{1.5} \xrightarrow[H_2O]{OH^-} CH_2{=}CH_2 + Si(OH)_4 + Cl^-$$

β-Chloro-*n*-propyltrichlorosilane in ether solution reacts vigorously with aqueous alkali at room temperature to give propylene.

$$CH_3CHClCH_2SiCl_3 \xrightarrow[H_2O]{OH^-} CH_3{-}CH{=}CH_2 + Si(OH)_4 + 4Cl^-$$

Acknowledgment.—We thank the Minnesota Mining and Manufacturing Co. and the Miner Laboratories for a grant which made this work possible.

Experimental

Reaction of β-Chloroethyltrichlorosilane with Methylmagnesium Bromide.—A 2-liter three-necked flask was fitted with a reflux condenser, mercury sealed stirrer and dropping funnel; the system was protected from moisture by a sulfuric acid trap. In the flask there was prepared, by the usual method, 3 equivalents of methylmagnesium bromide in 900 cc. of ether. The system was then connected to a trap maintained at −70° by acetone and Dry Ice. Next, a solution of 100 g., 0.5 mole, of β-chloroethyltrichlorosilane in 125 cc. of dry ether was added to the Grignard reagent which was cooled by means of an ice-bath; the time of addition was three hours. The ice-bath was removed and the reaction mixture heated

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[1] Paper IV. Sommer, Dorfman, Goldberg and Whitmore, THIS JOURNAL, 68, 488 (1946).

[2] Presented before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, September 12, 1944.

[3] Sommer and Whitmore, THIS JOURNAL, 68, 485 (1946) (Paper III).

[4] (a) This polymer contains a three-dimensional network of Si–O–Si bonds; (b) *cf.* Rochow and Gilliam, THIS JOURNAL, 63, 798 (1941).

on the steam-bath. A vigorous evolution of gas resulted. Part of this gas was absorbed by a solution of bromine in carbon tetrachloride which heated up and eventually decolorized. Fractionation gave 11.9 g. of ethylene dibromide. Thus ethylene is formed.

Next, the reaction product in the flask was hydrolyzed slowly by addition of 600 cc. of water and 250 cc. of concentrated hydrochloric acid. A low-boiling substance distilled into the Dry Ice trap during this operation. Fractionation of the 100 g. of material collected in the trap gave 30 g. of material b. p. 26°. Ethyl ether was removed from this latter material as follows: It was distilled into 50 cc. of cold concentrated sulfuric acid and the clear upper layer was in turn distilled into a flask cooled in a Dry Ice–acetone bath. This material, 24 g., $n^{20}\text{D}$ 1.3587, b. p. 26°, had the same physical constants as tetramethylsilane. Hence, the products of the reaction are tetramethylsilane and ethylene. The yield of tetramethylsilane based on the β-chloroethyltrichlorosilane was 55%.

Stepwise Addition of Methylmagnesium Bromide to β-Chloroethyltrichlorosilane.—In a 2-liter three-necked flask, equipped in the usual manner, there was placed 198 g., 1 mole, of β-chloroethyltrichlorosilane and 250 cc. of dry ether. One equivalent of methylmagnesium bromide was added slowly with stirring. Reaction took place, a quantity of white solid precipitating out, but no ethylene was given off even upon refluxing for one hour. Addition of the second equivalent of Grignard reagent followed by refluxing gave no evolution of ethylene. Addition of the third equivalent of Grignard gave a very small amount of ethylene. Addition of the fourth equivalent of methylmagnesium bromide gave a continuous evolution of ethylene which was converted to ethylene dibromide by a solution of bromine in carbon tetrachloride. There was obtained 37 g. of ethylene dibromide, b. p. 112.5°, $n^{20}\text{D}$ 1.5378.

Reaction of β-Chloroethyltrichlorosilane with Ethylmagnesium Bromide.—A solution of 300 g., 1.5 moles of β-chloroethyltrichlorosilane in 400 cc. of dry ether was cooled by an ice-bath and 7.6 equivalents of ethylmagnesium bromide were added during three hours. After stirring at room temperature for eleven hours, the reaction mixture was heated on the steam-bath. The evolved gas was passed through a solution of bromine in carbon tetrachloride. Fractionation of the carbon tetrachloride solution gave 12.5 g. of ethylene dibromide. After refluxing for five hours, the contents of the reaction flask were added to ice, followed by acidification to dissolve the basic magnesium salt. The ether layer was separated and the water layer extracted with two 250-cc. portions of ether. The ether solution of the product was dried with potassium carbonate and then fractionated. There was obtained 109 g., 0.75 mole, of tetraethylsilane, b. p. 153°, $n^{20}\text{D}$ 1.4278. This is a 50% yield based on the β-chloroethyltrichlorosilane.

Reaction of β-Chloroethyltrichlorosilane with Aqueous Alkali.—A 1-liter, three-necked round-bottomed flask was fitted with a mercury-sealed stirrer, reflux condenser, and dropping funnel. In the flask there was placed 400 cc. of 50% aqueous sodium hydroxide. Next, 100 g., 0.5 mole, of β-chloroethyltrichlorosilane was dissolved in 100 cc. of dry ether and added slowly to the aqueous alkali. There was a vigorous evolution of gas which decolorized a solution of 32 g. of bromine in 150 cc. of carbon tetrachloride. Distillation of this decolorized solution gave 36 g. of ethylene dibromide, b. p. 112°, $n^{20}\text{D}$ 1.5379. At the end of the addition there was present a clear upper ether layer and a clear water layer plus a small amount of gelatinous solid which was presumably silica.

Reaction of β-Chloro-*n*-propyltrichlorosilane with Aqueous Alkali.—A 2-liter three-necked flask was fitted with a mercury-sealed stirrer, reflux condenser, and dropping funnel. In the flask there was placed 400 cc. of 50% aqueous sodium hydroxide. Next, 106 g., 0.5 mole, of β-chloro-*n*-propyltrichlorosilane was dissolved in 100 cc. of dry ether and added slowly to the aqueous alkali. There was a vigorous evolution of gas which continued throughout the addition. It was found possible to condense most of the gas by passing it into ethyl ether maintained at −70° by traps cooled in Dry Ice–acetone. At the end of the addition, which took two hours, the cold ether solution of the gas was treated with a 50% solution of bromine in carbon tetrachloride until no further decolorization occurred. Fractionation of the ether solution yielded 51 g. of 1,2-dibromopropane, b. p. 141°, $n^{20}\text{D}$ 1.5203.

Synthesis of β-Chloroethyl Silicone.—A 2-liter three-necked round-bottomed flask was fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel. In the flask was placed 200 g. of ice and 500 cc. of water. To this was added 100 g., 0.5 mole, of β-chloroethyltrichlorosilane dissolved in 300 cc. of ether; addition was complete in one hour. The water layer was separated and the ether removed from the product by heating on the steam-bath. The product was a viscous glue-like material. This was heated for two hours at 170–180° leaving a white, brittle solid. The weight of solid polymer was 45 g., a yield of 80% based on the structure $ClCH_2CH_2SiO_{1.5}$. The polymer was analyzed for chlorine content as follows: Weighed samples, about 0.7 g., were fused with 15 g. of sodium peroxide and 1 g. of sucrose in a Parr bomb. The fusion was dissolved in distilled water and acidified with nitric acid. The resulting solution was titrated for chloride ion by the Volhard method.

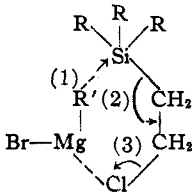
Anal. Calcd. for $C_2H_4ClSiO_{1.5}$: Cl, 30.7. Found: Cl, 31.0.

Properties of β-Chloroethyl Silicone.—Weighed samples, about 0.6 g., of the polymer were added to a mixture of 20 cc. of ethyl ether and 20 cc. of 0.5900 *N* alkali. When evolution of ethylene had ceased and the polymer was completely dissolved (due to formation of sodium silicate), the samples were back titrated with acid. The results were: calcd. for $ClCH_2CH_2SiO_{1.5}$; 30.7% Cl; found: 31.3% Cl.

A 300-cc., three-necked flask was fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel. In the flask there was placed 23 g., 0.2 mole, of β-chloroethyl silicone. To this was added 160 cc. of 10% aqueous sodium hydroxide. Addition was accompanied by a vigorous evolution of gas which decolorized a solution of 10 g. of bromine in 40 cc. of carbon tetrachloride. Fractionation yielded 11.3 g. of ethylene dibromide, b. p. 112°, $n^{20}\text{D}$ 1.5379.

Discussion

The fission of a C–Si bond by a Grignard reagent is a new reaction in organosilicon chemistry. It is due to the C–Cl bond beta to silicon. A possible mechanism for the ethylene-forming reaction involves a cyclic process



The beta C–Cl bond permits the formation of a Grignard coördination complex in which the alkyl group R′ of the Grignard reagent and the silicon atom are in the 1:6 position. The silicon atom acting as an electron sink[5] attracts the electron pair holding R′, as indicated by the broken arrow (1); electron displacements (2) and (3) occur simultaneously with this change. The process continues until the new bond R′–Si and MgX_2 are formed and ethylene is simultaneously elimi-

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(5) Whitmore and Sommer, This Journal, 68, 481 (1946) (Paper II).

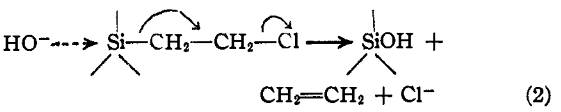
nated. The atomic electron shells remain complete throughout the change. A similar process obviously does not occur with alpha C–Cl bonds.

It should be emphasized that the reaction of a beta C–Cl bond with dilute alkali is not an ordinary hydrolysis, but is a 1:2 elimination reaction, similar in type to dehydrohalogenation, but involving a tetracovalent silicon atom instead of a combined hydrogen atom. It was shown above that small amounts of alkali accelerate β-eliminations involving silicon. β-Eliminations from alkyl halides which are favored by alkali take place by the following mechanism (E_2 elimination).[6]

$$Y \dashrightarrow H{-}CR_2{-}CR_2{-}Cl \longrightarrow YH + CR_2{=}CR_2 + Cl^- \qquad (1)$$

In these reactions a nucleophilic (electron donor) reagent Y, such as hydroxyl ion, attacks the proton (a combined hydrogen atom) resulting in the electron transfers indicated by the curved arrows. The hydrogen atom and the electron-attracting chlorine atom are bound to adjacent carbon atoms in the original molecule. The atomic electron shells remain complete throughout the change.

The reaction of a beta C–Cl bond in a silicon compound with alkali can be formulated similarly.



$$HO^- \dashrightarrow Si{-}CH_2{-}CH_2{-}Cl \longrightarrow SiOH + CH_2{=}CH_2 + Cl^- \qquad (2)$$

The only difference between the reactions is that in (2) the base attacks tetracovalent silicon instead of a combined hydrogen atom. In (2), just as in (1), the atomic electron shells remain complete throughout the change. Two bonds are broken, but each fission assists the other, the two together constituting a single synchronized process. It should be noted that the basic reagent might attack: (a) silicon attached to carbon, or (b) one of the two hydrogens attached to alpha carbon. Actually, the attack is exclusively on silicon, thus illustrating again the action of silicon as an electron sink.[5] As shown by the failure of primary alkyl halides to undergo dehydrohalogenation with dilute alkali, silicon attached to carbon takes part in β-eliminations far more readily than does hydrogen attached to carbon. A detailed discussion of the electronic interaction in a C–Si bond which is responsible for the behavior of silicon as an electron sink will be presented in a later paper.

Summary

1. β-Chloroethyltrichlorosilane and β-chloro-*n*-propyltrichlorosilane with aqueous alkali give ethylene and propylene, respectively. The extremely rapid reaction of beta C–Cl bonds with dilute alkali is not a hydrolysis, but a β-elimination, similar in type to the dehydrohalogenation of alkyl halides. It involves tetracovalent silicon instead of a combined hydrogen atom.

2. Reaction of β-chloroethyltrichlorosilane with methylmagnesium bromide gave ethylene and tetramethylsilane; ethylmagnesium bromide gave ethylene and tetraethylsilane.

STATE COLLEGE, PA. RECEIVED NOVEMBER 12, 1945

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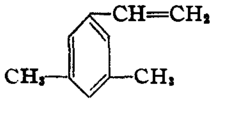
[6] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657–659 (1941); Skell and Hauser, THIS JOURNAL, **67**, 1661 (1945).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

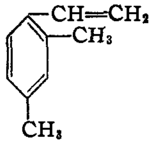
The Preparation and Polymerization of Four Isomeric Dimethylstyrenes[1,2]

BY C. S. MARVEL, J. H. SAUNDERS AND C. G. OVERBERGER

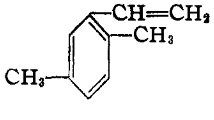
In order to investigate the effect of alkyl groups as substituents in styrene on its polymerization and on the properties of the polymer and copolymers this study of dimethylstyrenes has been made. This paper reports the synthesis of four of the isomeric dimethylstyrenes (I, II, III, IV) and gives a brief summary of the properties of their polymers. Copolymerization data will be reported in a later paper.



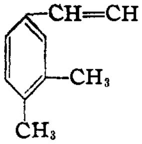
I



II



III



IV

3,5-Dimethylstyrene, 2,4-dimethylstyrene and 2,5-dimethylstyrene have been prepared previously by procedures other than those reported in this communication, but their characterization has been incomplete.

3,5-Dimethylstyrene (I)

This monomer was prepared by the following series of reactions.

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the twenty-second communication on vinyl polymers. For the twenty-first, see Marvel, Overberger, Allen, Johnston, Saunders and Young, THIS JOURNAL, **68**, 861 (1946).