chloride with sodium sulfide was inviting if suitable conditions could be found for causing it to take place. As expected, this reaction was very slow in aqueous or alcoholic solution. The use of ethylene glycol as a solvent gave a much more satisfactory procedure (see Experimental). The yield of bis-(2-ethylhexyl) sulfide from such a run was 76%.

As a further check on the usefulness of ethylene glycol as a solvent in the reaction of an organic chloride with sodium sulfide, a run was carried out employing 1,4-dichlorobutane. This reaction proceeded smoothly giving a 67% yield of tetramethylene sulfide.

Though our examples illustrating the usefulness of ethylene glycol as a solvent in the preparation of organic sulfides are limited, it appears likely that the method is of general applicability. Since we do not plan further investigation along this line, we feel it is desirable that we report our results for those who may find the method of interest.

EXPERIMENTAL

The starting materials were obtained from commercial sources and were used without purification. Boiling points are uncorrected. Fractionations were carried out through an 80-cm. Podbielniak-type column similar to that described by Cason and Rapoport.[4]

Bis(2-ethylhexyl) sulfide. A two-phase mixture of 74.3 g. (0.5 mole) of 2-ethylhexyl chloride, 60 g. (0.25 mole) of sodium sulfide nonahydrate, and 200 ml. of ethylene glycol was maintained at the boiling point (about 135°) under reflux for 24 hr. The course of the reaction was followed by removing a small sample of the upper phase from time to time to time and checking its refractive index. This property showed a moderately rapid increase during the early stages but had essentially ceased changing at the end of the heating period. At this point the upper layer was separated, washed twice with water, and dried over calcium chloride. Fractionation gave a forerun of about 10 g. of 2-ethylhexyl chloride, followed by 49 g. (76%) of nearly colorless product at 178–179° (23 mm.), n_D^{25} 1.4622.[5]

Anal. Calcd. for $C_{16}H_{34}S$: C, 74.34, H, 13.26, S, 12.40. Found: C, 74.46, H, 13.09, S, 12.24.

On a similar run to that described above, except that 200 ml. of ethanol was used in the place of the ethylene glycol, it was observed that the ethanol remained primarily in the upper phase with the alkyl chloride at the start of the reaction. As the reaction proceeded (reflux temperature, about 80°), the lower phase increased in volume and salts separated out, giving some tendency to bump. After a 24-hr. reflux period the reaction was worked up essentially as described above. Fractionation gave a forerun followed by 46 g. (71%) of bis(2-ethylhexyl) sulfide at 162–163° (12 mm.).

Tetramethylene sulfide. A mixture of 127 g. (1 mole) of 1,4-dichlorobutane and 240 g. (1 mole) of sodium sulfide nonahydrate was heated under reflux for 7 hr. The refractive index of the upper layer increased from n_D^{20} 1.4552 to n_D^{20} 1.4560 during this time, indicating very little reaction. At this point, 100 ml. of ethylene glycol was added and heating was continued for 16 hr. The refractive index of the upper layer (which was unchanged by the addition of the ethylene glycol since this component went into the lower phase) increased rapidly during this time to a final value of n_D^{20} 1.5038. At this point the upper layer was separated, washed twice with 20% sodium chloride solution, and dried over calcium chloride. Fractionation gave a yield of 59 g. (67%) of tetramethylene sulfide at 120–121°, n_D^{20} 1.5043 (lit.,[6] b.p. 121.2°, n_D^{20} 1.5047).

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[3] Since 2-ethylhexanol is commercially available, the method of preparation of sulfides utilized by F. Drahowzal and D. Klamann [*Monatsh.*, **82**, 970 (1951)] involving the reaction of an alkyl-4-toluenesulfonate with sodium sulfide was seriously considered. However, this would have involved the preparation of 2-ethylhexyl-4-toluenesulfonate as an intermediate, and was abandoned in favor of the direct reaction of the alkyl chloride with sodium sulfide.

[4] J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, N. Y., 1950, p. 238.

[5] On one run similar to that described here, except that no ethylene glycol was added, many hours of refluxing gave very little reaction. Fractionation of the top phase gave a recovery of 75% of the 2-ethylhexyl chloride and revealed no significant amount of the desired sulfide. A small forerun was not identified. When ethylene glycol was added to the run described above, it dissolved essentially completely in the sodium sulfide nonahydrate phase, giving a higher reflux temperature and possibly increasing the amount of alkyl chloride which dissolved in this phase.

[6] E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951) made use of the dibromide in the preparation of this compound.

The Polymerization and Cyclization of Allyldimethylsilane

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Mironov and Petrov have recently described[1] the synthesis and polymerization of certain silanes containing an unsaturated organic group and hydrogen joined to the same silicon atom. They reported, however, that they were unable to cause the polymerization of allyldimethylsilane under their experimental conditions (refluxing in the presence of 15% platinized carbon). We wish to report that we have successfully polymerized this monomer as well as effected the formation of a cyclic dimer from it.

Allyldimethylsilane was synthesized under high dilution conditions by a Grignard reaction, starting from dimethylchlorosilane, allyl bromide, and magnesium. The resulting monomer was heated under reflux, in the absence of solvent, with a 0.06% platinum-on-carbon catalyst.[2] Polymerization proceeded smoothly to yield a colorless, moderately viscous liquid, similar in appearance to the di-

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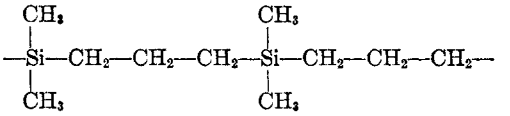
[1] V. F. Mironov and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 383 (1957).

[2] G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent **2,637,738**, May 5, 1953.

methylvinyl- and diethylvinyl- silane polymers described earlier.[3] In contrast with the previous results, the concurrent formation of a cyclic dimer was not observed.

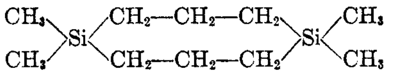
The structure of the new polymer was established by means of nuclear magnetic resonance spectral analysis, which showed that the silicon atoms in the main chain are joined through trimethylene bridges (I). In the NMR spectrum there was found a low, broad pattern of five lines caused by spin-spin coupling of the protons of the central methylene group in each bridge with the four protons of the two adjacent methylene groups. At slightly higher field there was also observed another resonance peak, which was attributed to methylene attached to silicon, and which was split into a triplet because of coupling with the protons of the central methylene group.



$$-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-CH_2-CH_2-$$

I

Since ring formation was not found to occur in the first experiment, a second reaction was conducted in the presence of toluene as a solvent in an effort to promote cyclization. Allyldimethylsilane polymer was formed as before, but in addition, a small amount of a crystalline material was isolated from the reaction mixture. The solid was identified as a cyclic dimer of allyldimethylsilane on the basis of elemental analysis, molecular weight determination, and a negative test for the Si-H function. The final proof of structure was by NMR analysis and was based on the same reasoning as that applied to the polymer, because it involved showing that the ring silicon atoms are connected through trimethylene bridges. The cyclic compound is therefore 1,1,5,5-tetramethyl-1,5-disilacyclo-octane (II), and as such it represents the first reported example of the 1,5-disilacyclo-octane ring system.



II

EXPERIMENTAL[4-6]

Allyldimethylsilane. A stirred slurry of 387.7 g. (15.95 gram atoms) of 70–80 mesh magnesium in 1250 ml. of dry ether was heated under vigorous reflux, while a mixture of 322.0 g. (2.66 moles) of allyl bromide and 251.7 g. (2.66 moles) of dimethylchlorosilane containing a trace of iodine was added dropwise through a high dilution apparatus.[7] The addition required 57 hr., following which the reaction mixture was stirred for an additional 15 hr. without external heating. An argon atmosphere was maintained throughout. The solid magnesium salts were removed by filtration and washed on the funnel with ether. The combined filtrate and ether washings were washed neutral with five 100-ml. portions of water, then dried over anhydrous sodium sulfate. Following the removal of solvent, the liquid residue was fractionated at atmospheric pressure to afford allyldimethylsilane, b.p. 69–70° (750 mm.), n_D^{25} 1.4042, yield 128.1 g. (48.0%). An analytical sample exhibited the following properties: b.p. 69.1° (750 mm.), n_D^{25} 1.4029, d_4^{25} 0.7046 (reported[1] b.p. 69° (755 mm.), n_D^{20} 1.4075, d_4^{20} 0.7086).

Anal. Calcd. for $C_5H_{12}Si$: C, 59.91; H, 12.07; MR_D, 34.63. Found: C, 59.88; H, 12.10; MR_D, 34.71.

Polymerization of allyldimethylsilane. A mixture of 21.6 g. (0.216 mole) of allyldimethylsilane and 0.22 g. of a 0.06% platinum-on-carbon catalyst was heated under reflux for 31 hr., during which time the reaction temperature rose from 67 to 153.5°. The polymer mass was allowed to cool to room temperature, ether was added, and the catalyst was removed by filtration. Following the removal of solvent from the combined filtrate and ether washings, the liquid residue was heated to 200° (20.5 mm.), then to 175° (0.28–0.32 mm.), but no volatile materials of any kind could be obtained. The cooled residue was filtered twice to effect clarification. The allyldimethylsilane polymer so obtained was a clear, colorless, moderately viscous liquid, n_D^{25} 1.4712, d_4^{25} 0.8549, yield 19.8 g. (91.7%).

Anal. Calcd. for $(C_5H_{12}Si)_x$: C, 59.91; H, 12.07; R_D, 0.3270. Found: C, 59.73; H, 11.87; mol. wt. (cryoscopic, in benzene), 1300; R_D, 0.3271.

Polymerization and cyclization of allyldimethylsilane. To 20.0 g. (0.200 mole) of allyldimethylsilane was added 0.20 g. of the Wagner platinum-on-carbon catalyst and 300 ml. of toluene. The mixture was heated under reflux for 72 hr., following which it was allowed to cool to room temperature, filtered to remove catalyst, then distilled to remove solvent. The solid and liquid components of the cooled distillation residue were separated by filtration. The filtrate consisted of clear, colorless, allyldimethylsilane polymer, n_D^{25} 1.4758, yield 15.6 g. (78.0%).

Anal. Found: Mol. wt. (cryoscopic, in benzene), 1160.

The solid substance remaining on the funnel was recrystallized repeatedly from ethanol to afford partially purified 1,1,5,5-tetramethyl-1,5-disilacyclo-octane (white needles), yield 0.6 g. (3.0%). An analytical sample, obtained by vacuum sublimation, exhibited m.p. 109.5–110.5° and gave a negative test for Si-H with ethanolic sodium ethoxide.

Anal. Calcd. for $C_{10}H_{24}Si_2$: C, 59.91; H, 12.07; mol. wt., 200. Found: C, 59.90; H, 11.90; mol. wt. (Rast), 220.

Nuclear magnetic resonance spectra. The nuclear magnetic resonance spectra were determined using the Varian Associates High Resolution Spectrometer (V-4300B), operated at 40 mc. and 9394.7 gauss.

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(3) J. W. Curry, *J. Am. Chem. Soc.*, **78**, 1686 (1956).

(4) Elemental analyses were performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

(5) Boiling and melting points are uncorrected.

(6) Calculated molar and specific refractivities were computed from bond refractivity values listed in the following references: A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *Chem. & Ind.* (*London*), 358 (1950), and A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

(7) N. J. Leonard and R. C. Sentz, *J. Am. Chem. Soc.*, **74**, 1704 (1952).