

at 3.90 Å (for gel from STC), at 4.09 Å (for gel from MTS) respectively, in good agreement with those of two polysiloxanes prepared by direct hydrolysis of STC and of MTS.

Anal. For STC gel (Calcd. for $n\text{SiO}_2$: Si, 46.75; Found: Si, 46.54), for MTS gel (Calcd. for $n\text{CH}_3\text{SiO}_{1.5}$: Si, 41.85; Found: Si, 41.57). No chlorine was detected by an argentometric titration carried out after ignition with sodium peroxide.

On shaking the red acetone with 5% sodium hydroxide solution, a deep red oily layer was separated at the top, from which mesityl oxide (b.p. 131°/760 mm., d_4^{25} 0.8535) was isolated; the distillation residue was a tar-like, black material from which no pure substances were isolated hitherto. It is considered to be a high order condensation product of acetone.

DDS. From DDS solution in acetone, when it contained not less than 5 moles of acetone per 1 mole of DDS, a colorless transparent oily layer separated at the bottom after standing for about 2 weeks. Fractional distillation under atmospheric pressure showed that it consisted of hexamethylcyclotrisiloxane (b.p. 134°/760 mm.), octamethylcyclotetrasiloxane (b.p. 175°/760 mm., n_D^{25} 1.3966) as the main products, and of higher polymers of dimethylsiloxane. The polymer fraction was very difficult to purify, because it gave no distillate below 200° under 2 mm. and its molecular weight changed (measured cryoscopically in benzene) on heating.

DPDS. From DPDS solution in acetone, hexaphenylcyclotrisiloxane (hereafter called trimer) crystallized upon standing. From a solution of suitable composition (e.g. DPDS, 8 g.; acetone, 25 g.; chloroform, 5 g.), trimer was obtained as large hexagonal plates of 5–10 mm. in width. Thorough investigations² on the relation between mixing ratio and yield of trimer, have been made recently in this laboratory. Properties of trimer produced here are as follows: m.p. 189°, d_4^{25} 1.23, mol. wt. 579–609 (in benzene).

Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{Si}_3\text{O}_3$: Si, 14.16; C, 72.68; H, 5.09. Found: Si, 14.06; C, 72.77; H, 4.83.

The X-ray powder pattern data are in complete agreement with those given by Hyde³ as type I₃ (trimer in orthorhombic system).

When non-purified acetone was used, the trimer was obtained much sooner (2 or 3 days after mixing, with the yield of 80% max.). These results would suggest that this "acetone method" is a convenient method for preparation of the trimer which is usually synthesized after the method of Burkhard.⁴

Reaction of other ketones. The author confirmed the statement by Rochow and Gingold⁵ that acetophenone did not react with any of the chlorosilanes. Methyl ethyl ketone was found to react with chlorosilanes used here in just the same manner of acetone, except that the siloxane formation was far slower and the color developed was a dark somewhat greenish red.

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Dicyclopropylmercury and Divinylmercury

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In the course of an investigation of the electrophilic cleavage of dialkylmercury compounds, two new mercury compounds, dicyclopropyl- and divinylmercury, were prepared in good yield by the action of mercuric chloride on the corresponding Grignard reagent in tetrahydrofuran.

It might be expected that since dialkylmercury compounds in general, with the exception of dimethylmercury, decompose on standing to give hydrocarbons and metallic mercury,² these compounds would exhibit considerable instability. However, dicyclopropylmercury stood for several weeks at room temperature exposed to sunlight without giving noticeable evidence of decomposition, while during the same period of time di-*n*-propylmercury showed considerable decomposition. Divinylmercury can be stored in the cold for several weeks without apparent decomposition, although over the same period of time at room temperature some deposition of mercury is detectable. It should be noted that although no previous preparation of divinylmercury has been reported, a series of substituted vinylmercury compounds were prepared and studied by Nesmeyanov and co-workers,³ and the vinylmercuric halides were recently prepared by reaction of tetravinyltin with the corresponding mercuric halides.⁴

The identities of the two compounds were established by their infrared spectra and carbon-hydrogen analysis. The spectrum of dicyclopropylmercury resembles that of cyclopropyl bromide⁵ with strong absorptions at 809, 880, 1030, and 2990 cm^{-1} . The spectrum of divinylmercury shows four strong absorptions at 938, 1010, 1250, and 2980 cm^{-1} , and two medium absorptions at 1400 and 3040 cm^{-1} . The absorption peaks at 2980 and 3040 cm^{-1} are attributed to CH stretching vibrations, those at 938 and 1010 cm^{-1} to CH_2 and CH out-of-plane deformation vibrations, and that at 1400 cm^{-1} to a CH_2 in-plane deformation vibration. The medium absorption peak at 1250 cm^{-1} is unaccounted for and appears also in the spectrum of dicyclopropylmercury.

This method of preparing the dialkylmercuries involving the addition of a tetrahydrofuran solution of mercuric chloride to a tetrahydrofuran solu-

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tion of the Grignard reagent is a general one, and seems to be much superior to their preparation in ether. Mercuric chloride is but slightly soluble in ether and is inclined to cake in the reaction mixture,⁶ while 100 g. of mercuric chloride can readily be dissolved in 100 ml. of tetrahydrofuran. Furthermore, prolonged periods of heating to obtain satisfactory yields⁷ are no longer necessary. In several attempts to prepare di-*n*-propylmercury in good yield in ether after the improved method of Gilman and Brown,⁸ the highest yield obtained was 57%. Marvel and Gould⁶ report a 51% yield of this compound in ether solution. A single trial using tetrahydrofuran gave a 75% yield of the di-*n*-propylmercury.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen. The tetrahydrofuran employed was predried over sodium hydroxide pellets and distilled from sodium wire.

Dicyclopropylmercury. Cyclopropylmagnesium bromide was prepared in tetrahydrofuran from magnesium turnings and cyclopropyl bromide, which was made according to the method of Roberts and Chambers.⁹ To 4.6 g. (0.19 mole) of magnesium in a 250 ml. 3-necked flask equipped with stirrer, water-cooled condenser, thermometer, and dropping funnel was added just enough tetrahydrofuran to cover the surface of the magnesium and approximately 3 ml. of cyclopropyl bromide. Reaction was thoroughly initiated by heating the solution to reflux for several minutes. The remaining 0.19 mole of cyclopropyl bromide, dissolved in 100 ml. of tetrahydrofuran, was added over a period of 1 hr. with the temperature of the reaction being held at 15–20° with an ice water bath to prevent coupling. Reaction was completed by heating the solution to between 50–60° for 1 hr.

To this Grignard solution was added dropwise with stirring a solution of 20.6 g. of mercuric chloride (80% of theory) in 50 ml. of tetrahydrofuran. After the addition was completed the solution was gently refluxed overnight. At the end of this time the solution was cooled and hydrolyzed with 50 ml. of water. Stirring was continued during the entire heating and hydrolysis. The liquid was separated from the pasty precipitate by suction filtration, the organic layer extracted with ether, washed with several portions of water, and dried over anhydrous magnesium sulfate. After preliminary stripping off of the organic solvent at atmospheric pressure using a water bath, the remaining liquid was transferred to a small distillation flask and vacuum distilled. 13.7 g. of dicyclopropylmercury was obtained (64% of theory), b.p. 110–112° at 18 mm.

Anal. Calcd. for C₆H₁₀Hg: C, 25.49; H, 3.57. Found: C, 25.56; H, 3.72.

Divinylmercury. Vinylmagnesium bromide was prepared from 30.4 g. (1.25 mole) of magnesium turnings and excess vinyl bromide in 500 ml. of tetrahydrofuran according to the method of Normant.¹⁰ To the Grignard solution in a 2-l. flask equipped as previously described was added dropwise a solution of 136 g. of mercuric chloride (80% of theory) in 200 ml. of tetrahydrofuran. Addition was accomplished over

a period of 1 hr. with stirring at a temperature of about 60°. After completion of addition the solution was heated for 1 hr. with stirring at 60° with an infrared lamp. The solution was then allowed to cool, and the remaining Grignard decomposed by hydrolysis with 250 ml. of water. Work-up proceeded as before with the exception that the organic solvent was separated from the rather volatile divinylmercury by use of a Rinco Rotary Evaporator. Using a water aspirator and a water bath at 30° the solvent came off at about 20 mm. The evaporation was discontinued when the pressure fell abruptly to 12–14 mm. The remaining liquid was distilled under vacuum through a 10 cm. Vigreux column by use of a water bath. 76.8 g. of divinylmercury (60% of theory) was obtained, b.p. 48–50° at 14 mm.

Anal. Calcd. for C₄H₆Hg: C, 18.86; H, 2.38. Found: C, 18.81; H, 2.58.

Because of its volatility, divinylmercury should be handled with extreme care in a good hood, as the dangerous toxicity of organomercury compounds is well known.¹¹ Divinylmercury readily decolorizes potassium permanganate solution while dicyclopropylmercury does not.

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Use of Chlorides in the Preparation of Organic Sulfides

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The reaction of alkyl bromides or iodides with sodium sulfide to give organic sulfides is well known.² Alkyl chlorides, though frequently more readily available than the bromides or iodides, are seldom employed.

Our research activities required a sample of bis-(2-ethylhexyl) sulfide. Since this material does not appear to be listed in the literature, we sought a method of preparation, preferably one suitable for scaling up, and which utilized commercially available intermediates. Since 2-ethylhexyl bromide and iodide were not readily available, the usual method of allowing an alkyl bromide or iodide to react with sodium sulfide in aqueous or alcoholic solution was not applicable.³ The reaction of 2-ethylhexyl

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