

of the oxidation only the formation is essential, which might well be followed by a decomposition whenever two molecules of the intermediate colide. With hydroquinone itself and its homologs, no compound of the type in question has been described. The suggestion that the semiquinone-quinone complex does not exist with the tetramethyl compound and is formed more easily the fewer methyl groups there are present in the molecule fits in well, however, with observations⁵ on the existence of dimeric quinhydrones.

Summary

An explanation is offered for the complicated non-linear dependence of the autoxidation rate of ψ -cumohydroquinone on the concentrations of ψ -cumoquinone and of oxygen which was found by James, Snell, and Weissberger.

(5) Michaelis, Schubert, Reber, Kuck and Granick, *THIS JOURNAL*, **60**, 1678 (1938).

A linear dependence in the region of low ψ -cumoquinone concentrations and a deviation from this dependence in the region of higher ψ -cumoquinone concentrations follows if the semiquinone intermediate reacts not only with oxygen but also with ψ -cumoquinone, and forms a product with the latter which disintegrates into ψ -cumohydroquinone and ψ -cumoquinone.

A quantitative formulation of this assumption gives the functional dependence of the reaction rate on the ψ -cumoquinone concentration and on the oxygen pressure, which is in excellent agreement with the experimental results.

The supposed complex is analogous to verdo-flavin. The presence of methyl groups in the molecule appears to have an influence on the formation of the complex which is similar to that on the stability of dimeric quinhydrones.

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Studies in Organo-silicon Synthesis. II. Reactions of Aryl Grignard Reagents with Silicon Halides

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In a preceding paper¹ it was demonstrated that hexaaryldisilanes are not formed from hexachlorodisilane by the Wurtz reaction. In view of this result it was thought to be of value to determine whether or not the Grignard reagent might be used successfully for this synthesis. When hexachlorodisilane was added to excess phenylmagnesium bromide in anhydrous ether and refluxed for two days, although a reaction occurred, no hexaphenyldisilane could be isolated, the final product being a brown tar, which probably resulted from the hydrolysis of the partially phenylated hexachlorodisilane.

A modification of this method was first used in 1933 by Cusa and Kipping² in the preparation of tetraphenyldisilane from silicon tetrachloride and phenylmagnesium bromide. It consisted of removing the ether by distillation after the reagents were well mixed, and heating the remaining solids

(1) Schumb, Ackerman and Saffer, *THIS JOURNAL*, **60**, 2486 (1938).

(2) Cusa and Kipping, *J. Chem. Soc.*, 1040 (1933). Although the procedure used often has been applied to the preparation of metal-organo compounds where higher temperatures are desired, we believe this was the first time it was employed in the synthesis of organo-silicon compounds.

at 160–180° for three to four hours. So far as we are aware, this case constitutes the only reported synthesis of a tetraarylsilane by means of the Grignard reagent. When this method was applied to the reaction of hexachlorodisilane and phenylmagnesium bromide, a good yield of hexaphenyldisilane was obtained, with only a trace of tetraphenyldisilane.

These results seem to disprove the findings of Schwarz and Sexauer,³ who reported that the reaction of phenylmagnesium bromide and hexachlorodisilane in the usual manner "formed no derivatives of disilane, instead the Si-Si bond was broken by the Grignard reagent, and a mixture of monosilane derivatives resulted." They reported also the isolation of diphenyldichlorosilane. If this substance had been formed in the first stage of our experiment, the heating process would have converted it into tetraphenyldisilane, of which we were unable to isolate more than a minute amount. In other experiments it was found possible to identify as little as 1% of tetraphenyldisilane in a mixture with hexaphenyldisilane. These facts,

(3) Schwarz and Sexauer, *Ber.*, **59B**, 333 (1926).

taken in conjunction with the good yields (40%) of hexaphenyldisilane obtained by us, indicate that the Si-Si bond is not ruptured in the reaction described.

Repetition of this experiment using *p*-tolylmagnesium bromide and hexachlorodisilane gave a 30% yield (on the basis of the Si_2Cl_6 used) of hexa-*p*-tolylidisilane, a compound hitherto undescribed in the literature. In order to test the effect of a change of the halogen in the silicon halide used in the reaction, phenylmagnesium bromide was caused to react with hexabromodisilane. Somewhat unexpectedly the main product of the reaction was found to be tetraphenylsilane, only a small amount of hexaphenyldisilane being formed. This result led us to determine the effect of further variation in the experimental conditions, using other silicon halides and also substances with different positions in the ring occupied, in order to ascertain the limitations of the method.

Condensations employing silicon tetrahalides were investigated first; the reaction between silicon tetrabromide and phenylmagnesium bromide was studied in order to note any difference due to the change of halogen from chloride to bromide. By carrying out the heating at 175–195°, a 60% yield of tetraphenylsilane was obtained, equivalent to that obtained by Cusa and Kipping² using silicon tetrachloride. As a variation of this method, in one experiment the simultaneous addition of silicon tetrachloride and bromobenzene in anhydrous ether to magnesium was employed with good results. The very vigorous reaction which ensued gave a final yield of 75% of tetraphenylsilane, and the time required was two hours less than that necessary for the usual method.

To test the effect of steric relationships in this synthesis, silicon tetrachloride was condensed with *p*-, *m*- and *o*-tolylmagnesium bromide and yields of 35, 8 and 0%, respectively, of the tetratolylsilanes were obtained, clearly showing the effect of steric hindrance, and likewise indicating that tetra-*o*-substituted phenylsilanes may not be prepared in this way.⁴

In an attempt to prepare an octaaryltrisilane, phenylmagnesium bromide and octachlorotrisilane

were condensed. The products of the reaction, however, were tetraphenylsilane and hexaphenyldisilane; no octaphenyltrisilane was found. It was thus concluded that octaaryltrisilanes could not be prepared by this procedure, because of the increased instability resulting from lengthening the silicon chain.

Since the Wurtz reaction had been shown to be inapplicable to the preparation of hexaaryldisiloxanes, containing the Si-O-Si configuration, from the corresponding halides,¹ the Grignard reaction again was employed to accomplish this purpose. Phenylmagnesium bromide was condensed with hexachlorodisiloxane, Si_2OCl_6 , and gave a 40% yield of hexaphenyldisiloxane, $\text{Si}_2\text{O}(\text{C}_6\text{H}_5)_6$. With the corresponding bromo derivative, Si_2OBr_6 , hexaphenyldisiloxane again was obtained, although here a small quantity of triphenylsilicol, $(\text{C}_6\text{H}_5)_3\text{SiOH}$, also was isolated. These facts indicate the greater instability in these reactions of Si_2OBr_6 as compared with Si_2OCl_6 . It was therefore to be expected that the corresponding reaction of the still less stable $\text{Si}_3\text{O}_2\text{Br}_8$ with phenylmagnesium bromide should yield larger amounts of the silicol. This conclusion was verified experimentally; triphenylsilicol was the sole product isolated.

The results of these experiments indicate that hexaaryldisilanes and hexaaryldisiloxanes may be prepared in fairly good yields from the corresponding silicon chlorides by the above-mentioned modification of the Grignard reaction. The reaction, however, cannot be extended to the preparation of compounds containing the Si-Si-Si or Si-O-Si-O-Si configurations, or of tetra-*o*-substituted phenylsilanes.

Inasmuch as this modification of the Grignard condensation gave good results in the synthesis of some aryl silanes, as above described, we next attempted the preparation by this method of certain hexaalkyldisilanes which could not be obtained in earlier work using the conventional procedure. Thus, although methyl⁵ and ethylmagnesium halides⁶ react readily with hexachlorodisilane in the usual Grignard method, yielding the corresponding hexaalkyldisilanes, hexapropyldisilane could not be isolated in this way. However, the modified Grignard method, employed with Si_2Cl_6 and propylmagnesium chloride, gave

(4) Tetra-*o*-tolylsilane is not reported in the literature. In an attempt to prepare this compound by the Wurtz reaction, silicon tetrachloride, *o*-bromotoluene and sodium were refluxed in boiling benzene for three days without formation of detectable quantities of tetra-*o*-tolylsilane.

(5) Bygden, *Ber.*, **46**, 707 (1912).

(6) In the study of the reaction of ethylmagnesium bromide and hexachlorodisilane the valued assistance of Mr. J. Ackerman, Jr., is acknowledged.

hexapropylidisilane, a compound hitherto undescribed in the literature.

Further work on the condensation of alkyl Grignard reagents with silicon halides, using this method, is in progress in this Laboratory.

Experimental

Reaction of Aryl Grignard Reagents with Silicon Halides.—In all experiments with the exception of the Barbier modification, the same general method was employed. Variations in the heating temperature, where employed, are noted in the following account. The Grignard reagent was prepared from the organic halide in anhydrous ethyl ether in a three-necked flask, outfitted with stirrer, condenser and dropping funnel, and an ether solution of the silicon halide was then added gradually with stirring. The mixture was refluxed and stirred for an hour, and the ether removed from the flask by distillation. The flask was then heated in an oil-bath at a temperature of 165–185° for four hours, during which time the brownish, semi-solid mass became a dry cake, usually of a light tan color. After cooling, the cake was broken up and decomposed with dilute hydrochloric acid, the resulting brownish tar steam-distilled to remove diaryls and the residue taken up in ether, from which the organo-silicon compound would readily settle out. It was then recrystallized from a suitable solvent, usually benzene.

I. Reactions with Si_2Cl_6 and Si_2Br_6 .—The Si_2Cl_6 used was of high purity, m. p. -1 to 0° , b. p. 90° at 125 mm. The Si_2Br_6 used had been purified by redistillation and melted sharply at 95° .

Reactions with Phenylmagnesium Bromide.—Ten grams of Si_2Cl_6 in 50 cc. of anhydrous ether was added to the Grignard reagent prepared from 55 g. of bromobenzene, an excess of about 30%; 7.5 g. of a white crystalline product was obtained, m. p. 341° (uncorr.). This was extracted with benzene at 40 – 50° , at which temperature hexaphenyldisilane is only slightly soluble. The extract yielded a small amount of a white solid, which on heating gave a trace of sublimate. The m. p. of this sublimate, 233° , corresponds to that of tetraphenylsilane.

On recrystallization of the main product from xylene, 7 g. of hexaphenyldisilane was obtained, corresponding to a yield of 40%.

Anal. Calcd. for $\text{Si}_2(\text{C}_6\text{H}_5)_6$: C, 83.35; H, 5.82. Found: C, 83.32; H, 6.20.

Thirty-five grams of Si_2Br_6 in 100 cc. of anhydrous ether was added to the Grignard reagent prepared from 85 g. of bromobenzene, an excess of 30%. Seventeen grams of a white crystalline product was isolated, m. p. 222° (uncorr.). By recrystallization from hot xylene 1 g. of hexaphenyldisilane, m. p. 345° (uncorr.), was obtained. The main product of the reaction appeared to be tetraphenylsilane, of which 15 g. was obtained after recrystallization from benzene, m. p. 232° .

Anal. Calcd. for $\text{Si}_2(\text{C}_6\text{H}_5)_6$: C, 83.35; H, 5.82. Found: C, 83.41; H, 6.01. Mol. wt. calcd. for $\text{Si}(\text{C}_6\text{H}_5)_4$, 336; found (camphor s. p.), 342, 330.

Preparation of Hexa-*p*-tolylidisilane.—Thirteen grams of Si_2Cl_6 in 50 cc. of anhydrous ether was added to the Grignard reagent prepared from 70 g. of *p*-bromotoluene.

The xylene extract of the reaction products yielded a white crystalline compound, m. p. 335° (uncorr.). After three recrystallizations from xylene 7 g. of hexa-*p*-tolylidisilane, m. p. 345° , was obtained, corresponding to a yield of 35%. The compound crystallizes in small, white plates and is similar in appearance to hexaphenyldisilane. It is insoluble in most organic solvents and in water, but is quite soluble in hot xylene and benzene. It is very stable, melting without decomposition, and it is not hydrolyzed by water or dilute sodium hydroxide.

Anal. Calcd. for $\text{Si}_2(\text{C}_7\text{H}_7)_6$: C, 83.68; H, 7.02; Si, 9.30. Found: C, 83.52; H, 7.12; Si, 9.10.

II. Reactions with SiBr_4 and SiCl_4 . Phenylmagnesium Bromide and SiBr_4 .—Eighteen grams of SiBr_4 in 50 cc. of anhydrous ether was added to the Grignard reagent prepared from 45 g. of bromobenzene, about 20% excess. Since at the usual heating temperature, 160 – 180° , the mixture still appeared liquid, the temperature was raised to 180 – 200° and kept there for four hours. By this means 10 g. of pure tetraphenylsilane was obtained, m. p. 232° , corresponding to a yield of 60%. Mol. wt. calcd. for $\text{Si}(\text{C}_6\text{H}_5)_4$, 336; found (camphor s. p.), 328, 339.

In the experiment employing the Barbier modification of the Grignard reaction, 6 g. of SiCl_4 and 30 g. of bromobenzene in 100 cc. of anhydrous ether were allowed to drop on magnesium turnings activated with a crystal of iodine. A vigorous reaction ensued, which yielded ultimately 8.8 g. of tetraphenylsilane, m. p. 232° , equivalent to a 75% yield. Mol. wt. calcd. for $\text{Si}(\text{C}_6\text{H}_5)_4$, 336; found (camphor s. p.), 339, 345.

Tolylmagnesium Bromides and SiCl_4 .—Ten grams of SiCl_4 was caused to react with the Grignard reagent prepared from 50 g. of *p*-bromotoluene, an excess of 25%. The reaction proceeded vigorously, and 7 g. of tetra-*p*-tolylsilane m. p. 226° , was obtained, a yield of about 30%. Mol. wt. calcd. for $\text{Si}(\text{C}_7\text{H}_7)_4$, 392; found (camphor s. p.), 381, 405.

Ten grams of SiCl_4 was condensed with the Grignard reagent prepared from 55 g. of *m*-bromotoluene, an excess of 35%. The reaction was not as vigorous as that preceding; 1.8 g. of tetra-*m*-tolylsilane, m. p. 148° , was isolated, corresponding to a yield of 8%. Mol. wt. calcd. for $\text{Si}(\text{C}_7\text{H}_7)_4$, 392; found (camphor s. p.), 371, 380.

Ten grams of SiCl_4 and the Grignard reagent prepared from 55 g. of *o*-bromotoluene were heated, after removal of the ether, at 160 – 180° , for three days. The brown tar resulting from the hydrochloric acid treatment of the products of the reaction failed to yield any tetra-*o*-tolylsilane.

III. Reaction with Si_3Cl_8 .—The Si_3Cl_8 used was purified material, b. p. 112 – 113° at 24 mm., 92 – 95° at 11 mm. Eighteen grams of Si_3Cl_8 in anhydrous ether was added to the Grignard reagent prepared from 80 g. of bromobenzene, an excess of 30%. A xylene extract of the products of the reaction yielded a white crystalline solid, m. p. 342° (uncorr.), which on recrystallization showed a m. p. of 355° and gave no depression in a mixed m. p. with a known sample of hexaphenyldisilane. It was, therefore, characterized as hexaphenyldisilane. By recrystallization of the rest of the material in the xylene extract, 2 g. of tetraphenylsilane, m. p. 231° , was obtained.

Anal. Calcd. for $\text{Si}_2(\text{C}_6\text{H}_5)_6$: C, 83.36; H, 5.83. Found: C, 83.30; H, 5.80.

IV. Reactions with the Silicon Oxyhalides.—The oxyhalides used were clear, colorless liquids of high purity, obtained by careful fractional distillation of some of the purest samples prepared in this Laboratory.⁷ The m. p. and b. p. of the oxyhalides were: Si_2OCl_6 , -35 and 137° at 760 mm.; Si_2OBr_6 , 28 and 81° at 1 mm.; $\text{Si}_3\text{O}_2\text{Br}_8$, 17 and 160° at 13 mm.

Reactions with Phenylmagnesium Bromide.—Six grams of Si_2OCl_6 in 30 cc. of anhydrous ether was condensed with the Grignard reagent prepared from 30 g. of bromobenzene, a 40% excess. The ether extract of the products yielded 5.5 g. of a white solid, m. p. 210° . This was recrystallized several times from benzene and white crystals, m. p. 221° , were obtained, which were identified as hexaphenyldisiloxane; yield 50%.

Anal. Calcd. for $\text{Si}_2\text{O}(\text{C}_6\text{H}_5)_6$: C, 80.90; H, 5.60. Found: C, 80.89; H, 5.47, 5.74.

Twenty grams of Si_2OBr_6 was allowed to react with the Grignard reagent prepared from 54 g. of bromobenzene, an excess of 30%. The main product of the reaction was hexaphenyldisiloxane, m. p. 220° , which was obtained in a 45% yield. By fractional crystallization of the main product in benzene a very small amount (0.1–0.15 g.) of triphenylsilicol, $(\text{C}_6\text{H}_5)_3\text{SiOH}$, m. p. 145° , was obtained.

Anal. Calcd. for $\text{Si}_2\text{O}(\text{C}_6\text{H}_5)_6$: C, 80.90; H, 5.60. Found: C, 80.93; H, 5.72.

Twenty-five grams of $\text{Si}_3\text{O}_2\text{Br}_8$ was added to the Grignard reagent prepared from 60 g. of bromobenzene, an excess of 30%. The reaction was very sluggish and a temperature of 180 – 200° was maintained in the heating bath in order to ensure the most complete reaction possible. The sole product which we were able to isolate from the reaction mixture was triphenylsilicol, m. p. 150° .

Anal. Calcd. for $(\text{C}_6\text{H}_5)_3\text{SiOH}$: C, 78.22; H, 5.84; mol. wt., 276. Found: C, 78.03; H, 5.63; mol. wt. (benzene s. p.), 256.

Reactions of Alkyl Grignard Reagents with Hexachlorodisilane. I. Reaction of Ethylmagnesium Bromide and Si_2Cl_6 .—Twenty grams of Si_2Cl_6 in 80 cc. of anhydrous ether was added gradually with stirring to the Grignard reagent prepared from 55 g. of pure ethyl bromide. After the addition of the Si_2Cl_6 the mixture was stirred and refluxed for two hours, when it became semi-solid. Employing the conventional procedure, the Grignard reagent was then decomposed with dilute hydrochloric acid and the ether layer containing the alkylsilanes separated. After several fractional distillations a very small fraction, b. p. 152° , identified as tetraethylsilane, was isolated. Mol. wt. calcd. for $\text{Si}(\text{C}_2\text{H}_5)_4$, 144; found (cyclohexane s. p.), 134, 136. A 9-g. fraction, b. p. 250° , was characterized as hexaethylidisilane, and corresponded to a yield of 50%. Mol. wt. calcd. for $\text{Si}_2(\text{C}_2\text{H}_5)_6$, 230; found (cyclohexane s. p.), 239.

II. Reaction of *n*-Propylmagnesium Chloride and Si_2Cl_6 .—When Si_2Cl_6 and *n*-propylmagnesium chloride were

caused to react in the usual manner, *i. e.*, as in the preceding case with ethylmagnesium bromide, oils were obtained, which despite intense purification gave consistently anomalous C–H analyses. The modified technique was therefore employed. Fifteen grams of Si_2Cl_6 was added to the Grignard reagent prepared from 50 g. of *n*-propyl chloride. After thorough stirring and refluxing for an hour, the ether was removed by distillation, and the remaining solids heated at 160 – 180° for four hours. Fractional distillation of the reaction products gave a large yield of an oil, which, after shaking with sulfuric acid, boiled at 114° at 3 mm., and was characterized as hexa-*n*-propyldisilane, a colorless oil, insoluble in water and reagent alcohol; soluble in benzene, ether, cyclohexane and absolute alcohol; n_{D}^{20} 1.4740; d_4^{20} 0.8693.

Anal. Calcd. for $\text{Si}_2(\text{C}_3\text{H}_7)_6$: C, 68.72; H, 13.5; Si, 17.8; mol. wt., 314. Found: C, 68.01; H, 12.9; Si, 17.5; mol. wt. (cyclohexane s. p.), 297.

A very small fraction of tetra-*n*-propylsilane was also obtained, b. p. 212° , mol. wt. calcd. for $\text{Si}(\text{C}_3\text{H}_7)_4$, 200; found (cyclohexane s. p.), 190.

Summary

1. Reactions of aryl Grignard reagents with silicon halides in the conventional manner were found to yield only partially substituted silanes. The following halides were studied: SiCl_4 , Si_2Cl_6 , Si_3Cl_8 , Si_2OCl_6 , SiBr_4 , Si_2Br_6 , Si_2OBr_6 , $\text{Si}_3\text{O}_2\text{Br}_8$.

2. The high temperature modification of the Grignard reaction was shown to be applicable to the preparation of both aryl and alkyl hexasubstituted disilanes, and of aryl hexasubstituted disiloxanes.

3. Except in the case of the tetrahalides, silicon chlorides were found to be preferable to the bromides in these syntheses, since the bromine derivatives always gave some fission products. Si_3Cl_8 , however, failed to yield any octaaryltrisilanes, thus demonstrating anew the comparative instability of the >Si-Si-Si< configuration.

4. Tetra-*o*-substituted phenylsilanes could not be prepared by this synthesis.

5. Hexa-*p*-tolylidisilane, a white crystalline solid, stable toward water or dilute sodium hydroxide, melting without decomposition at 345° , and hexa-*n*-propyldisilane, a colorless oil, b. p. 114° at 3 mm., likewise stable toward hydrolysis, were prepared.

(7) Schumb and Klein, *THIS JOURNAL*, **59**, 261 (1937).