2-aminobenzenephosphonic acid. Repeated fractional crystallization of the amino acid mixture from water resulted in isolation of the 3-isomer, in the form of colorless needles, which decomposed at 290–292° (heated block); this product gave no detectable amounts of tribromoaniline on treatment with bromine water. The 2-isomer could not be freed of the 3-isomer completely and the material always gave small amounts of the abovementioned tribromoaminobenzenephosphonic acid with bromine water, in addition to the normally expected tribromoaniline; this imperfect material showed a decomposition range of 294–296° (heated block).

Hydrolysis of the mixed diethyl nitrobenzenephosphonates (20 g., 0.0775 mole) by boiling with concentrated hydrochloric acid (175 ml.) for five hours resulted in isolation of 11–12.5 g. (78.5–89.5%) of the free acid mixture, which after crystallization from benzene–ether–ligroin mixture melted at 138–139°. This mixture, in the form of fine, almost colorless needles, could not be resolved into its components by crystallization. Reduction with alkaline sulfide, according to the previously described procedure,[6] gave the amino acid mixture similar to the one described above.

Acknowledgment.—The writer wishes to express his gratitude to Professor R. L. Shriner, who pointed out some time ago the possibility of non-homogeneous nature of Nijk's nitrobenzenephosphonic acid.

Summary

Nitration of diethyl benzenephosphonate results in the formation of appreciable amounts of the *o*-nitro isomer, along with the *m*-nitro isomer.

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[6] Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Some Steric Effects of the Cyclohexyl Group in Organosilicon Compounds

BY W. H. NEBERGALL[1,2] AND O. H. JOHNSON

In earlier studies[3,4] the writers found that chlorotricyclohexylgermane, $(C_6H_{11})_3GeCl$, was the sole product of the action of a large excess of cyclohexyllithium upon germanium tetrachloride, no tetracyclohexylgermane apparently being formed. However, the halogen atom of this substituted germane was found to be replaceable by normal alkyl, benzyl and phenyl groups. Attempts to substitute the chlorine atom by the sterically hindered isopropyl, cyclohexyl and *o*-tolyl groups were unsuccessful.

Efforts to prepare tricyclohexylphenylsilane, $(C_6H_{11})_3SiC_6H_5$, by the action of a large excess of cyclohexylmagnesium bromide on phenyltrichlorosilane were reported as unsuccessful by Cusa and Kipping.[5] Instead of the expected tricyclohexyl derivative, they obtained dicyclohexylphenylsilane, $(C_6H_{11})_2SiH{\cdot}C_6H_5$. This compound was brominated and then alkylated, using ethylmagnesium bromide at 160–180° to form dicyclohexylphenylethylsilane. The failure to obtain tricyclohexylphenylsilane was attributed to the steric effect associated with the cyclohexyl group.

These results led the authors to investigate the extent of substitution of the cyclohexyl group in the silane molecule by the use of cyclohexyllithium upon silicon tetrachloride. Under conventional experimental conditions three cyclohexyl groups are substituted for chlorine atoms in the reaction of cyclohexyllithium in large excess with silicon tetrachloride.

$$3C_6H_{11}Li + SiCl_4 \longrightarrow (C_6H_{11})_3SiCl + 3LiCl$$

The reaction of the tricyclohexylsilicon compound, however, differed from its germanium analog in that efforts to replace the chlorine atom by methyl, ethyl and phenyl groups were unsuccessful.

$$(C_6H_{11})_3SiCl + RLi \longrightarrow \text{No reaction}$$

Both Grignard and organolithium compounds were employed as alkylating agents and the ether was replaced by higher boiling solvents in an endeavor to force the reaction. In addition, since the Si–Br bond is reported[6] as weaker than the Si–Cl bond, bromotricyclohexylsilane was prepared and its alkylation attempted but still no evidence of further substitution was observed.

Chlorotricyclohexylsilane failed to respond to sodium condensation in boiling toluene, whereas bromotricyclohexylgermane condensed to form hexacyclohexylgermane,[3] $(C_6H_{11})_3Ge{-}Ge(C_6H_{11})_3$, under similar conditions.

Chlorotricyclohexylsilane was reduced to tricyclohexylsilane, $(C_6H_{11})_3SiH$, by lithium aluminum hydride in ether solution. This silane was brominated and iodinated to form the corresponding halides. Hydrolysis of the chloride yielded tricyclohexylsilanol, $(C_6H_{11})_3SiOH$, which was esterified by boiling with acetic anhydride to form acetoxytricyclohexylsilane.

Experimental

Synthesis of Chlorotricyclohexylsilane Using Cyclohexyllithium.—Cyclohexyllithium was prepared by adding, over a period of four hours, 95 g. (0.8 mole) of chlorocyclohexane to 500 ml. of low-boiling petroleum ether containing an excess of lithium metal shot in a one-liter, three-necked flask fitted with a mercury-sealed, air-driven stirrer, a reflux condenser protected by a calcium chloride tube, and a dropping funnel containing the chlorocyclohexane. The reaction mixture was stirred and heated on a warm water-bath to initiate the reaction, after which

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[1] Part II from a thesis submitted by W. H. Nebergall to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. See THIS JOURNAL, **71**, 1720 (1949), for Part I.

[2] Present address: Indiana University.

[3] Johnson and Nebergall, THIS JOURNAL, **70**, 1706 (1948).

[4] Johnson and Nebergall, *ibid.*, **71**, 1720 (1949).

[5] Cusa and Kipping, *J. Chem. Soc.*, 1040 (1933).

[6] Linus Pauling, "The Nature of the Chemical Bond," 2d ed., Cornell University Press, Ithaca, New York, 1940, p. 53.

the heat of reaction caused continuous refluxing for two hours after all of the chlorocyclohexane had been added. Without filtering out the lithium chloride and excess lithium, 17.0 g. (0.1 mole) of silicon tetrachloride in 50 ml. of petroleum ether was added dropwise to the solution of cyclohexyllithium which was stirred and cooled in an ice-water-bath during the entire addition. After allowing the reaction mixture to stand overnight at room temperature, the lithium chloride and excess lithium were filtered out and the excess cyclohexyllithium was destroyed with 6 *N* hydrochloric acid while the reaction mixture was stirred and cooled in an ice-water-bath. The organic layer was separated, dried over anhydrous calcium chloride, and the solvent was removed by distillation leaving a viscous oily liquid. The product which was crystallized from glacial acetic acid and recrystallized from petroleum ether proved to be chlorotricyclohexylsilane, $(C_6H_{11})_3SiCl$, m. p. 101–102°,[7] yield 15 g. (60%).

Anal. Calcd.: Si, 8.97. Found: Si, 8.8.

Attempted Preparation of Methyltricyclohexylsilane by the Grignard Method.—Methylmagnesium iodide was prepared by treating 3 g. (0.13 mole) of magnesium turnings with 14.2 g. (0.1 mole) of methyl iodide in 150 ml. of absolute ether. On completion of the reaction, 3.1 g. (0.01 mole) of chlorotricyclohexylsilane dissolved in 20 ml. of dry toluene was added to the Grignard reagent. The reaction mixture was refluxed for one hour and then the uncombined ether was replaced by dry toluene. After heating the mixture on a steam-bath for three hours, the Grignard reagent was destroyed by pouring the reaction mixture into a mixture of cracked ice and dilute hydrochloric acid. The organic layer was separated and dried over anhydrous calcium chloride. The toluene was removed by air evaporation, yielding 2.5 g. of colorless crystals, which were recrystallized from low-boiling petroleum ether; m. p. 100–101°. A test for the chloride ion following hydrolysis with alcoholic potassium hydroxide was positive, indicating that the original chlorotricyclohexylsilane had undergone no change.

Attempted Substitution of Chlorotricyclohexylsilane Using Organolithium Compounds.—Methyllithium was prepared from 14.2 g. (0.1 mole) of methyl iodide and an excess of lithium metal shot in 150 ml. of anhydrous ethyl ether by the general procedure outlined for the preparation of cyclohexyllithium. On completion of the reaction, 3.1 g. (0.01 mole) of chlorotricyclohexylsilane dissolved in 25 ml. of ether was added to the solution of methyllithium. The mixture was brought to the reflux temperature and held there for two hours. The ethyl ether was replaced by petroleum ether (50–60°) and the reaction mixture was refluxed overnight. After hydrolyzing the methyllithium with dilute hydrochloric acid, the ether layer was separated and the ether was removed by evaporation. The product, recrystallized from glacial acetic acid, melted at 100–101°; test for the chloride ion was positive following hydrolysis with alcoholic potassium hydroxide. Again the methyl group failed to replace the chlorine atom of chlorotricyclohexylsilane.

Using similar procedures, attempts were made to replace the chlorine atom with ethyl and phenyl groups by the organolithium method. In each case, failure was encountered.

Suspecting that the resistance of the chlorine to substitution might be due to the stability of the Si-Cl bond, the less stable bromo derivative was prepared and an attempt was made to alkylate it, using ethyllithium. Once again, bromotricyclohexylsilane was reclaimed, unaltered, at the end of the experiment.

An Attempt to Synthesize Hexacyclohexyldisilane.—A solution of 6 g. of chlorotricyclohexylsilane in 100 ml. of dry toluene was heated with an excess of metallic sodium in a 200-ml., three-necked flask, fitted with a reflux condenser and adapted for flushing with nitrogen. The mixture was held at the reflux temperature for four hours during which time no indications of a reaction were apparent. The toluene solution was then removed from the sodium and upon evaporation of the solvent, 5.8 g. of the original chlorotricyclohexylsilane was reclaimed; m. p. 100–101°; test for the chloride ion was positive.

Reduction of Chlorotricyclohexylsilane by Lithium Aluminum Hydride.—A solution of 6 g. (0.019 mole) of chlorotricyclohexylsilane in 50 ml. of anhydrous ethyl ether was added dropwise to an excess of lithium aluminum hydride in 100 ml. of ethyl ether contained in an apparatus adapted for refluxing and excluding moisture. The reaction mixture was refluxed for one-half hour and then the ethyl ether was replaced by low-boiling petroleum ether. The excess lithium aluminum hydride and the chlorides of lithium and aluminum as products of the reaction are insoluble in petroleum ether, whereas the desired product, tricyclohexylsilane is soluble. After warming the petroleum ether solution, the insoluble substances were filtered out and most of the petroleum ether was removed by distillation at atmospheric pressure and the rest of the ether was taken off under reduced pressure. The tricyclohexylsilane, $(C_6H_{11})_3SiH$, obtained was an oily liquid which boiled at 183–185° (9 mm.), $n^{25}D$ 1.5132, yield 5 g. (90%). The compound did not freeze in a bath of Dry Ice and ethanol.

Anal. Calcd.: Si, 10.08. Found: Si, 10.0.

Bromination of Tricyclohexylsilane.—A solution of 1 g. of this silane in 50 ml. of carbon tetrachloride was treated with a slight excess of bromine. A carbon tetrachloride solution of the bromine was added dropwise to the silane solution until the bromine color no longer disappeared and the formation of hydrogen bromide ceased. The reaction mixture was heated to boiling for a few minutes and then the product was crystallized by air evaporation of the solvent. The yield of bromotricyclohexylsilane, $(C_6H_{11})_3SiBr$, m. p. 112–113°, was quantitative.

Anal. Calcd.: Si, 7.85. Found: Si, 7.9.

Iodination of Tricyclohexylsilane.—A sample of 2.8 g. of this compound was dissolved in 50 ml. of carbon tetrachloride and a slight excess of iodine crystals was added to the solution. The reaction mixture was refluxed for two hours, at the end of which time hydrogen iodide ceased to be evolved. The excess iodine was removed by combining it with powdered antimony and filtering. The carbon tetrachloride was replaced by low-boiling petroleum ether and the product, $(C_6H_{11})_3SiI$, was crystallized from this solvent and recrystallized from absolute ethanol; m. p. 97–98°, yield 2.1 g. (52%).

Anal. Calcd.: Si, 6.94. Found: Si, 7.0.

Iodotricyclohexylsilane appears to be quite unstable in view of the fact that samples of the crystalline product soon turn brown and its solutions take on a violet coloration on exposure to the air.

The Hydrolysis of Chlorotricyclohexylsilane.—A sample of 10 g. (0.032 mole) of this chloride was dissolved in 200 ml. of boiling, 5% alcoholic potassium hydroxide. Immediately a white precipitate of potassium chloride began to form and the reaction was complete in a few minutes. An equal volume of water was added to the solution which caused the formation of a white precipitate of tricyclohexylsilanol, $(C_6H_{11})_3SiOH$. This product was filtered out, crystallized from ethyl ether, and recrystallized from low-boiling petroleum ether; m. p. 176–177°, yield 8.2 g. (87%).

Anal. Calcd.: Si, 9.53. Found: Si, 9.4.

The Esterification of Tricyclohexylsilanol.—A solution of 3 g. (0.01 mole) of this silanol in 20 ml. of acetic anhydride was held at the reflux temperature for two hours. The solution was then cooled in an ice-water-bath and upon agitation of the mixture, a crop of colorless crystals formed. The product was collected on a sintered-glass filter crucible and washed with ethanol. The dried crystals melted at 82–83° and analysis indicated acetoxytricyclohexylsilane, $(C_6H_{11})_3Si—OCOCH_3$, yield 2.7 g. (80%).

Anal. Calcd.: Si, 8.34. Found: Si, 8.5.

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[7] All melting points are uncorrected.

Summary

1. It has been found that cyclohexyllithium in large excess reacts with silicon tetrachloride to form chlorotricyclohexylsilane but no tetracyclohexylsilane.

2. Attempts to replace the chlorine atom of chlorotricyclohexylsilane by methyl, ethyl and phenyl groups using both Grignard and organolithium compounds as alkylating agents failed. In addition, this chlorosilane failed to respond to sodium condensation to give the disilane. These results may be due to the steric properties of the three cyclohexyl groups attached to the silicon atom in chlorotricyclohexylsilane.

3. Six new compounds have been prepared and some of their properties described. These compounds are: chlorotricyclohexylsilane, bromotricyclohexylsilane, iodotricyclohexylsilane, acetoxytricyclohexylsilane, tricyclohexylsilane and tricyclohexylsilanol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Photochemical Studies of the Porphyrins. II. The Photoöxidation of Chlorins by Various Quinones

BY FRANK M. HUENNEKENS[1] AND M. CALVIN

Calvin and Dorough[2] have previously established that zinc tetraphenylchlorin is photooxidized in the presence of quinones to zinc tetraphenylporphin. This reaction was studied in great detail for 1,2-naphthoquinone and the following observations made: (1) There is no dark complex formed between the quinone and chlorin. (2) Light adsorbed by the chlorin (6225 Å.) is required. (3) Oxygen inhibits the reaction. (4) The reaction rate is directly independent to the light intensity and inversely related to the temperature. (5) The reaction rate is independent of the naphthoquinone concentration in the range 10^{-3} to 10^{-6} *M*. (The chlorin concentration is initially about 10^{-5} *M*.) (6) A function of the chlorin concentration gives a straight line when plotted against time.

This work has now been extended to include both ortho- and para-quinones (eight in all), as well as measurements on magnesium tetraphenylchlorin.

Experimental

Part 1. Apparatus.—The apparatus and methods were essentially the same as those employed by Calvin and Dorough. The reader is referred to the preceding paper in this series for complete details.[2]

Light Source.—The actinic light was obtained from the tungsten filament lamp (operated at 9 volts) and the monochromator system of a Beckman Quartz Spectrophotometer, Model DU. With the wave length set at 6225 Å. and the slit width at 0.8 mm. the spectral segment was 28.8 Å. In the case of certain para-quinones the reaction was slow; this necessitated focussing the Beckman lamp with great care so that an appreciable reaction could be observed in a matter of a few hours.

Light Intensity Measurements.—After the lamp had been on for at least thirty minutes, the thermostatted cell compartment and phototube housing were removed and a small thermopile (without window) was placed at a fixed, reproducible distance from the front face of the Beckman. At this distance the light beam had an area of 1.77 sq. cm.; the opening of the thermopile was centered in this beam. The intensity of the beam was determined at the beginning and end of each run and the average computed for the mid-point of that run. The thermopile and galvanometer were calibrated with a U. S. Bureau of Standards radiation lamp; the sensitivity was found to be 119.4 watts/sq. cm./cm. deflection. Using the same principles as in the previous paper[2] but with slightly different constants I_0 (in photons/sec.) may be calculated from the galvanometer deflection, D (in cm.), by the following equation: $I_0 = 6.56 \times 10^{14} \times D$.

Reaction Vessel.—The reaction vessel was an ordinary 1-cm. square Pyrex mandrel cell with a magnetic stirrer and an evacuation stopcock built into the cell top (see Fig. 6, reference (2)).

Temperature Control.—Scrupulously clean water, maintained in a large thermostat at 25.0 ± 0.1°, was circulated slowly through the modified Beckman cell compartment with quartz windows. The top of the reaction cell above the water was enclosed in a light-proof cover and heated by a stream of hot air to *ca.* 40°; the heating prevented the benzene solution in the evacuated cell from distilling and condensing on the stirring motor in the upper part of the cell.

Routine Procedure.—In the dark the quinone and chlorin solutions in benzene were mixed: 2.56 cc. of the resultant solution was delivered via a calibrated overflow cup to the reaction cell. The ground glass connection between the top and the bottom of the cell was susceptible to leaks due to striations in the grease caused by the heat and mechanical vibrations of the stirrer. This was remedied by using Cello-Grease No. 14-637, manufactured by the Fisher Scientific Company; the product is guaranteed to maintain its consistency up to 120°. Perfect seals were obtained as follows: The ground glass surfaces at the joint were heated and a thin film of melted grease applied with a brush. The joint was clamped together under light pressure and allowed to cool for thirty minutes. The cell and solution were de-oxygenated by the method of freezing the assembly in liquid nitrogen and evacuating the cell. After thawing the solution, purified hydrogen (passed over hot copper according to the method of Michaelis)[3] was admixed with the vapor phase and the process repeated. Six sweepings with hydrogen were used.

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[2] Calvin and Dorough, THIS JOURNAL, **70**, 699 (1948), Paper I of this series.

[3] Michaelis in "Physical Measurements of Organic Chemistry," Vol. II, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1946, p. 1096.