

References

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**Preparation and Properties of *p*-Trimethylsilyl-phenyl-dichlorophosphine,
p-Me₃SiC₆H₄PCl₂**

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*Manuscript received 22 March 1972; revised 10 July 1972;
accepted 5 February 1973.*

AROMATIC carbon-silicon bond is more reactive than the aromatic carbon-hydrogen bond under identical electrophilic reaction conditions and this has been thoroughly discussed by Dey¹⁻³ and its synthetic utility has been emphasized^{1,2} and demonstrated³. This note describes a very interesting desilylation reaction (see ref. No. 1 for this nomenclature) which leads to the formation of a novel organosilicon compound, *p*-trimethylsilyl-phenyl-dichlorophosphine, *p*-Me₃SiC₆H₄PCl₂.

Experimental

p-Bistrimethylsilylbenzene was prepared by a previously published method⁴. Solvents and chemicals were purified by usual procedures. The liquid product was purified by fractional distillation through a 70 cm (or, 80 cm) precision vigreux column of low hold up. Boiling point (uncorrected) and refractive indices quoted were those of middle fractions. The purity of the isolated compounds was checked by GLC. Elemental analyses of the compounds were carried out by the Microanalysts of Sussex University, England. Infrared spectra were recorded in nujol and hexachlorobutadiene and liquid film using a Perkin Elmer 257 Infrared Grating Spectrophotometer. Proton N.M.R. spectra were recorded on a varian A60 instrument using TMS as internal standard.

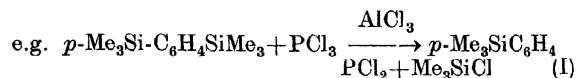
Preparation of p-trimethylsilyl-phenyl-dichlorophosphine, P-Me₃SiC₆H₄PCl₂: (The reaction was carried out in an atmosphere of dry nitrogen).

A mixture of phosphorus trichloride (3 ml.) and anhydrous aluminium chloride (5.3 g; 0.04*M*) was stirred for about 1 hr at room temperature. To this

stirred mixture was then added dropwise a solution of *p*-bistrimethylsilylbenzene (6.6 g; 0.03*M*) in 30 ml. of phosphorus trichloride. After the addition, the reaction mixture was stirred for half an hour at room temperature, then refluxed for 3 hr. After this period, phosphorus oxychloride (6.1 g 0.04*M*) was added while the mixture was hot. The whole mixture was then stirred half an hour, whereby granular complex, AlCl₃.POCl₃ was settled down. It was filtered off, and the filtrate on fractionation gave *p*-trimethylsilyl-phenyl-dichlorophosphine (I) in 80% yield, b.p. 60°-62°/0.2 mm. *n*_D²⁵ 1.5888 (Found: C, 42.98; H, 5.11%; SiC₉H₁₃PCl₂ requires: C, 43.02; H, 5.18%). The IR spectrum showed the expected peaks at 1265 cm⁻¹(S), 860 cm⁻¹(S), 772 cm⁻¹(S) (Me₃Si); 1135 cm⁻¹(S) (Ph-Si); 1445 cm⁻¹(m) (Ph-P); 825 cm⁻¹(S) (*p*-C₆H₄). The NMR spectrum showed resonances at 9.75τ (Me₃Si) and 2.05-2.80τ (C₆H₄), with the expected integration pattern.

Results and Discussion

Phosphinyldesilylation apparently occurs when *p*-bis-trimethylsilylbenzene reacts with phosphorous trichloride in presence of anhydrous aluminium chloride to form (I) and is comparable with normal aromatic electrophilic substitution.



Electron-withdrawing effect of dichlorophosphine (PCl₂) group or a complex of AlCl₃ with—PCl₂ group or a combined effect of both the phenomena might deactivate the other Me₃Si group present in the para-position, which possibly explains the selective cleavage of one Me₃Si group by dichlorophosphine group. Preparation of this type of organosilicon compounds by other means is very difficult, and thus demonstrates the usefulness of phosphinyldesilylation in preparative chemistry.

The presence of Me₃Si group in the compound (I) is proved by infrared and proton-NMR spectral studies (see experimental). The very strong band observed in infrared spectrum of (I) at 1265 cm⁻¹ may be considered as symmetrical CH₃ deformation⁵⁻⁹ and a very weak peak at 1420 cm⁻¹ may be considered as asymmetrical CH₃ deformation⁵⁻⁹. The two strong bands at 860 cm⁻¹ and 772 cm⁻¹ is due to Si-CH₃ stretching vibrations⁵⁻⁹. Phenyl-silicon vibration observed at 1135 cm⁻¹,⁵⁻⁹ while phenyl-phosphorous at 1445 cm⁻¹.¹⁰ The para-aromatic substitution is indicated by a strong peak at 825 cm⁻¹. The proton-NMR spectral studies also supports the presence of Me₃Si group in (I). The methyl protons (in Me₃Si group) signal appears at 9.75τ, whereas the phenyl protons signal appears in between 2.05-2.80τ. The former is a singlet, whereas the latter is found to be very complex in nature. The position of the methyl proton signal in (I) is lowered about 0.2τ in comparison with the methyl proton signal in *p*-Me₃SiC₆H₄SiMe₃.

The mechanistic aspects of this type of electrophilic desilylations have been discussed previously by Dey¹ and Normal and Taylor¹¹.

Other phosphinyldemetallation reactions are now being done with a view to study the reactivities of PCl_2 group for the possible synthesis of novel organo-metallic and organic compounds.

Acknowledgement

Some of the work was done at Sussex University, England. Thanks are due to Prof. C. Eaborn, F.R.S. and Dr. D. R. M. Walton for laboratory facilities and useful discussion.

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Chelate Polymers of 5,8-Dihydroxy Quinoxaline and 2,5-Dihydroxy *p*-Benzoquinone

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Manuscript received 4 April 1972; revised 26 December 1972;

accepted 5 February 1973

WE have reported our studies on the chelate polymers of cobalt with various dihydroxy quinones¹ and of cobalt with 2,5-dihydroxy *p*-benzoquinone and amine². We now present the preparation of the chelate polymers of 2,5-dihydroxy *p*-benzoquinone and amine with nickel and of 5,8-dihydroxy quinoxaline with copper, nickel and cobalt and study of their electrical resistivity.

Experimental

2,5-dihydroxy *p*-benzoquinone (BQH_2): It was prepared by the oxidation of hydroquinone³.

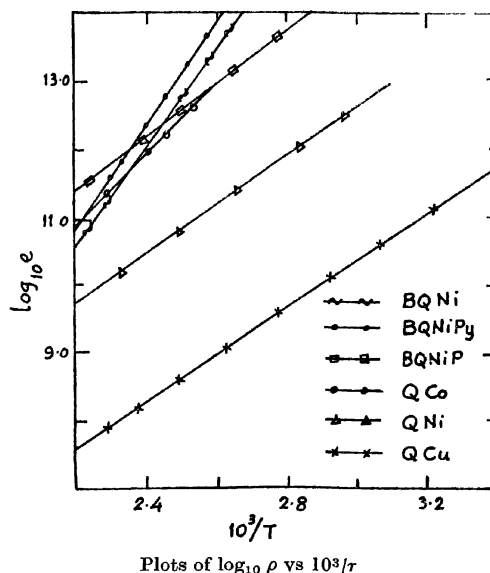
Nickel polychelates (BQNi , BQNiPy , BQNiP): Nickel chloride, dissolved in alcohol, was added dropwise to the calculated amount of BQH_2 in alcohol in absence of or in presence of an amine (pyridine or *p*-phenylene diamine). Stirring of the mixture was continued for 3 hr. The mixture was then refluxed for 2 hr and left overnight. The precipitates were filtered, washed with alcohol and ether and dried. They are insoluble in water and organic solvents.

5,8-Dihydroxy quinoxaline (QH_2): It was prepared from hydroquinone as follows: Hydroquinone was nethylated by the method of Bogert and Howells⁴ so that 1,4-dimethoxy benzene was obtained. It was nitrated by the method of King, Clark and Davis⁵. A mixture of 2,3- and 2,5- dinitro 1,4-dimethoxy benzene was obtained and was used directly for reduction by sodium dithionite in aqueous alcohol. The mixture was refluxed for 1 hr on water bath, to convert it into a mixture of diamino derivatives. On boiling off excess alcohol, neutralisation and dilution with water, 2,5-diamino 1,4-dimethoxy benzene crystallised out. It was filtered off and from the filtrate 2,3-diamino 1,4-dimethoxy benzene was extracted with chloroform. It was converted into 5,8-dimethoxy quinoxaline by the method of Adachi⁶ and then demethylated to 5,8-dihydroxy quinoxaline by the method of King, Clark and Davis⁵.

Chelate Polymers (QNi , QCo , QCu): Metal acetate dissolved in dimethyl formamide with a few drops of acetic acid was added dropwise to the calculated amount of QH_2 dissolved in dimethyl formamide; the mixture was stirred for two hours and left overnight. The precipitates were filtered, washed with dimethyl formamide, alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The colour, m.pt., analysis, etc. of these chelate polymers are presented in table 1.

Electrical Resistivity: Electrical resistivity of these chelate polymers was determined over a temperature range using Ellico's million meg-ohmmeter model RM-70. The results are shown graphically in Fig. 1.



Discussion

On the basis of analysis, the chelate polymers BQNi , BQNiPy and BQNiP are formulated as a linear chain (I) where *aq* and *am* represent water and amine respectively. Similarly the chelate polymer