

for  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_6)_3$ , favoring the conclusions we arrived at in a previous paper.<sup>3</sup>

We thank Prof. G. Natta and Prof. R. Ercoli for their helpful suggestions.

(3) P. Corradini and G. Allegra, *THIS JOURNAL*, **81**, 5510 (1959).

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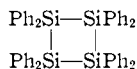
RECEIVED FEBRUARY 25, 1960

### THE REACTION OF DICHLORODIPHENYLSILANE WITH SODIUM

Sir:

One of the reactions examined by Kipping and co-workers in their extensive studies with organosilicon compounds was that of dichlorodiphenylsilane with sodium.<sup>1</sup> When the reaction was carried out above the melting point of sodium without solvent, or with toluene or xylene as solvent, a complex mixture of chlorine-free organosilicon compounds resulted. This mixture was resolved into six components after a painstaking series of operations. One of these designated as Compound (A) first was reported not to melt at 300° and later was reported to melt at 335°. This sparingly soluble compound was crystallized from benzene and gave satisfactory analyses for a compound having four diphenylsilylene groups,  $[(\text{C}_6\text{H}_5)_2\text{Si}]_4$ . Several possible structures were considered, and of these the one given preference on the basis of apparent unsaturated characteristics of Compound (A) was that containing "two trivalent silicon atoms":  $-\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{Ph}_2\text{Si}-$ .

Incidental to a study concerned with cyclic organosilicon compounds, we have examined Compound (A), and have found that it does not contain any trivalent silicon atoms and that the high reactivity or "unsaturation" characteristics may be explained by a cyclic structure

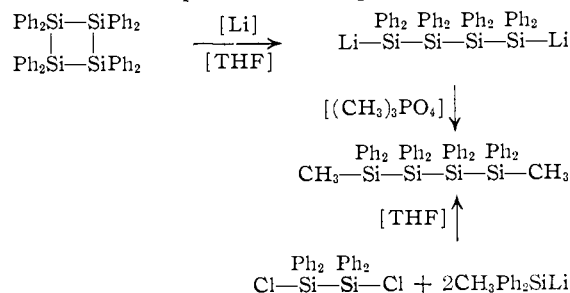


This octaphenylcyclotetrasilane undergoes ready cleavage by lithium in tetrahydrofuran to give a novel organosilicon compound containing two silyllithium groups. The di-silyllithium compound reacts with trimethyl phosphate to give 1,4-dimethyloctaphenyltetrasilane which melts at 223° after crystallization from a 1:1 mixture of benzene and petroleum ether (b.p. 50–60°).

*Anal.* Calcd. for  $\text{C}_{50}\text{H}_{46}\text{Si}_4$ : C, 79.09; H, 6.11; Si, 14.8. Found: C, 79.16 and 79.11; H, 6.41 and 6.24; Si, 14.85 and 14.72. Hydrogen value (moist piperidine): calcd., 101; found, 103, 104.

The same dimethyl compound was obtained from either 1,4-dichlorooctaphenyltetrasilane<sup>2</sup> or 1,4-

dibromoöctaphenyltetrasilane,<sup>2</sup> and methylolithium. Also, and most significantly, the dimethyl compound was obtained by the reaction of 1,2-dichlorotetraphenyldisilane and methylidiphenylsilyllithium, two compounds of unequivocal structure.



The exclusion of the biradical or trivalent silicon structure was confirmed by the measurements of J. H. Chaudet and Dr. W. D. Kennedy. The compound when examined by electro paramagnetic resonance both in the solid state and as a saturated solution in toluene failed to give a free radical resonance. The sensitivity for the detection of free radicals by the electro paramagnetic resonance is of the order of  $10^{15}$  unpaired electrons per gram of compound. It should also be stated that the octaphenylcyclotetrasilane lacked sufficient solubility for a nuclear magnetic resonance examination.

**Acknowledgments.**—The authors are grateful to J. H. Chaudet, and Dr. W. D. Kennedy, of the Tennessee Eastman Co., for the electron paramagnetic resonance studies. This research was supported in part by the United States Air Force under contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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RECEIVED MARCH 2, 1960

### PRIMARY PHOSPHINE OXIDES

Sir:

Tertiary phosphine oxides were prepared early in the history of organophosphorus chemistry and are now accessible by a number of methods.<sup>1</sup> Oxides of secondary phosphines were discovered much later, and general methods of preparation have come to light only recently.<sup>2–4</sup> We wish to report here the first preparations of primary phosphine oxides.

These substances were observed initially as products of the reaction of phosphine with ketones. Our work indicates that this apparently general reaction takes the course indicated, which involves transfer of oxygen from carbon to phosphorus in the first step.

(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 98.

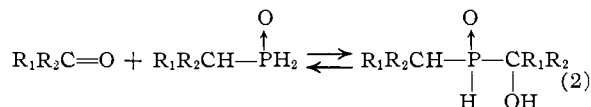
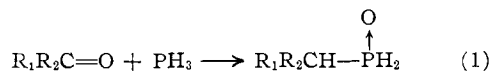
(2) R. H. Williams and L. A. Hamilton, *THIS JOURNAL*, **74**, 5418 (1952).

(3) R. H. Williams and L. A. Hamilton, *ibid.*, **77**, 3411 (1955).

(4) M. M. Rauhut, I. Hechenbleikner, H. A. Currier and V. P. Wystrach, *ibid.*, **80**, 6690 (1958).

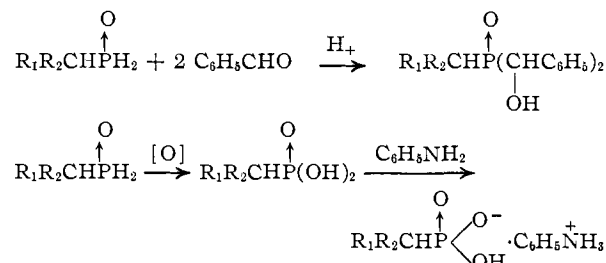
(1) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 and 848 (1921); F. S. Kipping, *ibid.*, **123**, 2590 and 2598 (1923); F. S. Kipping, *ibid.*, **125**, 2291 (1924); F. S. Kipping, 2719 and 2728 (1927); F. S. Kipping and H. E. Murray, *ibid.*, 360 (1929); A. R. Steele and F. S. Kipping, *ibid.*, 2545 (1929); and F. S. Kipping, "The Bakerian Lecture," *Proc. Roy. Soc.*, **159A**, 139 (1937).

(2) The dichloro and dibromo compounds were prepared from compound (A) and tetrachloroethane and ethylene bromide, respectively. A later report will describe these and a wide variety of other reactions of the octaphenylcyclotetrasilane as well as a corrected formula for "Compound B" formed from it.



The reactions were conducted by allowing solutions of the ketones in concentrated hydrochloric acid to react with phosphine until no more of the latter was absorbed. Examination of the resulting solutions by n.m.r. spectroscopy in the phosphorus region indicated that a mixture of the corresponding primary phosphine oxide and hydroxy secondary phosphine oxide was formed in all cases.<sup>5</sup> These ketones are ranked in the order of increasing amounts of primary phosphine oxides obtained in reaction with phosphine: cyclohexanone < cyclopentanone < acetone < 2-pentanone < 2-heptanone < 3-pentanone < acetophenone < 4-heptanone. Thus, the relative amounts of the two products obtained is determined largely by steric effects, which govern the extent to which the second reaction takes place.

Some of the primary phosphine oxides were isolated as low melting solids but proved to have poor stability. These substances were, therefore, converted to their benzaldehyde adducts and phosphonic acid oxidation products (isolated as aniline salts) for characterization. The hydroxy

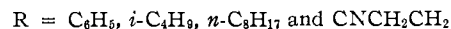
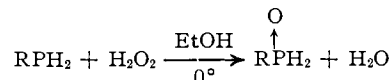


secondary phosphine oxides were obtained as stable crystalline solids in several cases. As an illustration, reaction of phosphine with acetone gave both the primary and secondary oxides. Isopropylphosphine oxide was identified by its conversion to bis-( $\alpha$ -hydroxybenzyl)-isopropylphosphine oxide, m.p. 162–163° (*Anal.* Calcd. for  $C_{17}H_{21}O_3P$ : C, 67.09; H, 6.96; P, 10.18. Found: C, 66.73; H, 7.17; P, 9.89); and to the aniline salt of isopropylphosphonic acid, m.p. 175–177° (*Anal.* Calcd. for  $C_9H_{16}NO_3P$ : C, 49.76; H, 7.43; P, 14.26. Found: C, 49.34; H, 7.21; P, 14.07). The other product was (1-hydroxy-1-methylethyl)-isopropylphosphine oxide, m.p. 71–72.5°. *Anal.* Calcd. for  $C_6H_{15}O_2P$ : C, 47.99; H, 10.07; P, 20.63. Found: C, 47.73; H, 9.78; P, 20.19.

A more widely applicable method of preparing primary phosphine oxides was found in the con-

(5) We wish to express our appreciation to Dr. J. E. Lancaster for the n.m.r. studies. Hydroxy secondary phosphine oxides gave a 1-1 doublet centered near -60 p.p.m. (referred to 85%  $H_3PO_4$ ) while the primary oxides gave a 1-2-1 triplet centered near -15 p.p.m. The splittings (P-H coupling) were about 28 p.p.m., which is in good agreement with those of other organic compounds having the >P(O)H structure which have been studied in this laboratory. The doublet indicates one hydrogen attached to P; the triplet indicates two.

trolled oxidation of primary phosphines. Several primary phosphine oxides were obtained in this way in good yields using stoichiometric amounts of hydrogen peroxide. These substances were



characterized by n.m.r. spectroscopy and by the preparation of derivatives as in the case of the phosphine-ketone products. Octylphosphine oxide was isolated as a crystalline solid of limited stability, m.p. 46–48°. It was much more stable in solution and could be heated at 75° in ethanol for a period of several hours without appreciable decomposition. Treatment with acrylonitrile and a trace of sodium methoxide gave bis-(2-cyanoethyl)-octylphosphine oxide, m.p. 66–68°, identical with a specimen obtained by an alternate route.<sup>6</sup> Treatment with benzaldehyde in HCl solution gave bis-( $\alpha$ -hydroxybenzyl)-octylphosphine oxide, m.p. 127–129°. *Anal.* Calcd. for  $C_{22}H_{31}O_3P$ : C, 70.56; H, 8.35; P, 8.27. Found: C, 70.63; H, 8.21; P, 8.18.

The chemistry of primary phosphine oxides will be described in greater detail in a forthcoming publication.

(6) M. M. Rauhut, unpublished work. The material was prepared by reaction of 1-octene and bis-(2-cyanoethyl)-phosphine oxide using a free-radical initiator.

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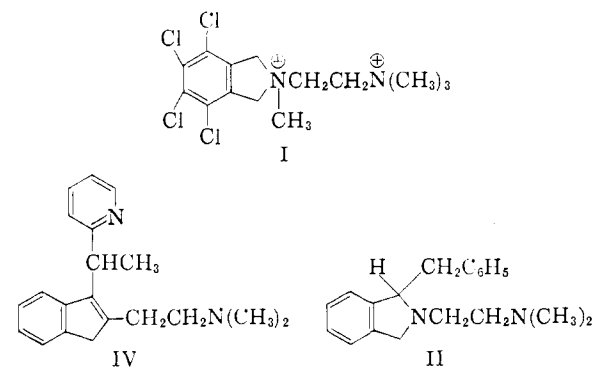
SHELDON A. BUCKLER  
MARTIN EPSTEIN

RECEIVED FEBRUARY 27, 1960

#### A NEW CLASS OF HIGHLY ACTIVE ANTIHISTAMINICS

Sir:

Since 1952 our laboratory has been interested in isoindolines and related substances derived by the reduction of cyclic imides. One outcome of this work was the ganglionic blocking drug, chlorisondamine (I). Among a large number of widely



related substances, 1-benzyl-2-(2-dimethylaminoethyl)-isoindoline (II) (*Anal.* Found for  $C_{19}H_{24}N_2 \cdot 2HCl \cdot 0.5H_2O$ : C, 63.28; H, 7.79; N, 7.64), m.p. 200–201°, was prepared by the sequence to be given. Benzaldehyde was treated with dimethylaminoethylamine to give 3-benzylidene-2-(2-dimethylaminoethyl)-phthalimidine