759. *Organosilicon Compounds. Part XXI.* Some Compounds Containing Phosphorus.*

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Organosilicon compounds containing phosphorus have been prepared, including phosphonates [*e.g.*, $PhMe_2Si{\cdot}CH_2{\cdot}P(O)(OBu^n)_2$], phosphine oxides [*e.g.*,(p-$MeC_6H_4Me_2{\cdot}Si{\cdot}CH_2)_3PO$], phosphates [*e.g.*, ($p$-$Me_3Si{\cdot}C_6H_4{\cdot}O)_3PO$], and a phosphinic acid (p-$Cl{\cdot}C_6H_4Me_2{\cdot}Si{\cdot}CH_2)_2P(O){\cdot}OH$.

INTEREST attaches to organosilicon compounds containing phosphorus because of the possibility of modifying the properties of Silicones (particularly lubricating power and flame-resistance) by introduction of phosphorus-containing groups. We have prepared several compounds containing silicon attached to phosphorus through carbon or carbon and oxygen. A few such compounds have been reported previously.[1-5]

Interaction of the appropriate organosilylmethyl halides with sodium salts of the type $NaP(O)(OR)_2$ has been used to give the phosphonates $Me_3Si{\cdot}CH_2{\cdot}P(O)(OR)_2$ (R = n-C_4H_9, n-C_5H_{11}), $ArMe_2Si{\cdot}CH_2{\cdot}P(O)(OBu^n)_2$ (Ar = Ph, p-$Me{\cdot}C_6H_4$, and p-$Cl{\cdot}C_6H_4$), and $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}P(O)(OBu^n)_2$. The products are liquids, stable enough to be fractionally distilled at reduced pressure.

The solid phosphine oxides $(Me_3Si{\cdot}CH_2)_3PO$ and (p-$Me{\cdot}C_6H_4Me_2{\cdot}Si{\cdot}CH_2)_3PO$ have been prepared from the appropriate $\geqslant Si{\cdot}CH_2{\cdot}MgCl$ compound and phosphorus oxychloride in ether. The same reaction involving the Grignard reagent p-$Cl{\cdot}C_6H_4Me_2{\cdot}Si{\cdot}CH_2{\cdot}MgCl$ gave only the phosphinic acid, (p-$Cl{\cdot}C_6H_4Me_2{\cdot}Si{\cdot}CH_2)_2P(O){\cdot}OH$.

The phosphates $(Me_3Si{\cdot}CH_2{\cdot}O)_3PO$ (a liquid stable to distillation at reduced pressure) and (p-$Me_3Si{\cdot}C_6H_4{\cdot}O)_3PO$ (a solid) were prepared from phosphorus oxychloride and the

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* Part XX, *J.*, 1957, 955.

[1] Frisch and Lyons, *J. Amer. Chem. Soc.*, 1953, **75**, 4078.

[2] Gilbert and Precopio, Abs. Papers, 125th Meeting of the American Chemical Society, 1954, p. 16N; Gilbert, U.S.P. 2,768,193/1956; *Chem. Abs.*, 1957, **51**, 5816.

[3] Keeber and Post, *J. Org. Chem.*, 1956, **21**, 509.

[4] Chernyshev and Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 282; *Chem. Abs.*, 1956, **50**, 11,283.

[5] Seyferth, *J. Amer. Chem. Soc.*, 1958, **80**, 1136.

sodium salts of trimethylsilylmethanol and *p*-trimethylsilylphenol in ether. Use of the latter salt with dimethylphosphorochloridate similarly gave the compound *p*-$Me_3Si{\cdot}C_6H_4{\cdot}OP{\cdot}(O)(OMe)_2$.

Tristrimethylsilylmethylphosphine oxide decomposes in nitrogen at 270°, hexamethyldisiloxane probably being a product. Di-n-butyl trimethylsilylmethylphosphonate decomposes with polymerization on boiling at atmospheric pressure.

EXPERIMENTAL

General.—In fractional distillations special precision-made Vigreux columns (*ca.* 15 theoretical plates) were used.

(*Aryldimethylsilyl*)*methyl Chlorides.*—These were made by boiling the appropriate ArMgBr compounds with chloro(chloromethyl)dimethylsilane in ether for 12 hr., and had the following properties: (Ar =) Ph, b. p. 134—137°/48 mm.; *p*-$Me{\cdot}C_6H_4$, b. p. 120—122°/12 mm., 136—138°/26 mm. (previously [6] reported incorrectly as 138—140°/12 mm.); *p*-$Cl{\cdot}C_6H_4$, b. p. 102—104°/3 mm. (previously [6] reported incorrectly as 133°/3 mm.), n_D^{20} 1·5342.

Phosphonates.—Bromomethyltrimethylsilane (1 mol.) was boiled for 12 hr. with a light petroleum (b. p. 60—80°) solution of sodium (1 mol.) in dialkyl hydrogen phosphite (1 mol.). Washing with water followed by fractionation gave di-n-butyl trimethylsilylmethylphosphonate [3] (25%), b. p. 154—158°/17 mm., or *di-n-pentyl trimethylsilylmethylphosphonate* (36%), b. p. 186—188°/18 mm., n_D^{20} 1·4418 (Found: C, 55·0; H, 11·0. $C_{14}H_{33}O_3PSi$ requires C, 54·5; H, 10·8%). Similarly from (chloromethyl)pentamethyldisiloxane, with 23 hr. of refluxing (but with filtration to remove sodium chloride instead of washing), was obtained *di-n-butyl pentamethyldisiloxanylmethylphosphonate* (23%), b. p. 150—152°/10 mm., n_D^{20} 1·4251 (Found: C, 46·9; H, 9·7. $C_{14}H_{35}O_4PSi_2$ requires C, 47·4; H, 9·9%).

Similarly from aryl(chloromethyl)dimethylsilanes were prepared di-n-butyl aryldimethylsilylmethylphosphonates as follows: (aryl =) *phenyl* (40%), b. p. 200—202°/10 mm., n_D^{20} 1·4864 (Found: C, 59·6; H, 9·5. $C_{17}H_{31}O_3PSi$ requires C, 59·6; H, 9·1%); p-*chlorophenyl* (11%), b. p. 186·5—188°/2 mm., n_D^{20} 1·4942 (Found: C, 54·5; H, 8·4. $C_{17}H_{30}O_3ClPSi$ requires C, 54·2; H, 8·0%); p-*tolyl* (32%, in this case refluxing was for 36 hr.), b. p. 187—189°/2·6 mm., n_D^{20} 1·4879 (Found: C, 60·3; H, 9·2. $C_{18}H_{33}O_3PSi$ requires C, 60·6; H, 9·3%).

Diethyl trimethylsilylmethylphosphonate,[2] b. p. 118·5—121°/22 mm., was obtained in 25% yield by refluxing together equimolecular quantities of bromomethyltrimethylsilane and triethyl phosphite until the temperature rose from 96° to 120° (5 days), and then fractionating. Diethyl pentamethyldisiloxanylmethylphosphonate [2] (41%), b. p. 154—156°/36 mm., was prepared similarly from chloromethylpentamethyldisiloxane by refluxing for 42 hr., during which the temperature of the mixture rose from 153° to 195°.

Phosphine Oxides.—Phosphorus oxychloride (14 g., 0·092 mole) in ether (50 ml.) was added slowly, with cooling to −5°, to the Grignard reagent from magnesium (6·7 g., 0·28 g.-atom) and bromomethyltrimethylsilane (4·6 g., 0·27 mole) in ether (150 ml.), and the mixture was boiled for 13 hr. After the usual hydrolysis procedure the ether layer was evaporated to dryness and the residue was recrystallised from ethanol, to give tristrimethylsilylmethylphosphine oxide (14·5 g., 51%), m. p. 182° (Found: C, 47·0; H, 10·9. Calc. for $C_{12}H_{33}OPSi_3$: C, 46·7; H, 10·8%). (This compound was recently prepared by a different route.[5])

Similarly from chloromethyldimethyl-*p*-tolylsilane and *p*-bromophenyltrimethylsilane, respectively, but with 18 hours' refluxing, were obtained *tris*(*dimethyl*-p-*tolylsilylmethyl*)*phosphine oxide*, m. p. 111·5° (from ethanol) (Found: C, 67·3; H, 8·6. $C_{30}H_{45}OPSi_3$ requires C, 67·1; H, 8·45%), and tris-(*p*-trimethylsilylphenyl)phosphine oxide, m. p. 259° (from ethanol) (cf. ref. 1). A similar procedure involving chloromethyl-*p*-chlorophenyldimethylsilane gave only *bis*-(p-*chlorophenyldimethylsilylmethyl*)*phosphinic acid*, m. p. 95° (from ethanol) (Found: C, 50·4; H, 5·9. $C_{18}H_{25}O_2Cl_2PSi_2$ requires C, 50·1; H, 5·85%).

An attempt to prepare tris(pentamethyldisiloxanylmethyl)phosphine oxide by this method was unsuccessful, an unidentified solid of m. p. 140° being obtained (Found: C, 29·0; H, 10·2%).

Phosphates.—Sodium (3·5 g., 0·15 g.-atom.) was dissolved in trimethylsilylmethanol (15 g., 0·15 mole) in ether (100 ml.), phosphorus oxychloride (7·7 g., 0·05 mole) in ether (50 ml.) was added, and the mixture was boiled for 16 hr. After filtration, the residue was distilled and the

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[6] Eaborn and Jeffrey, *J.*, 1954, 4266.

distillate fractionated to give ***tristrimethylsilylmethyl phosphate*** (3·2 g., 18%), b. p. 134—136°/5 mm., n_D^{20} 1·4331 (Found: C, 40·7; H, 9·4. $C_{12}H_{33}O_4PSi_3$ requires C, 40·4; H, 9·3%).

Similarly from *p*-trimethylsilylphenol (but without distillation of the product) was obtained *tris*-p-*trimethylsilylphenyl phosphate* (64%), m. p. 99° (from ethanol) (Found: C, 59·8; H, 7·4. $C_{27}H_{39}O_4PSi_3$ requires C, 59·7; H, 7·25%), and from *p*-trimethylsilylphenol (0·1 mole) and dimethyl phosphorochloridate (0·1 mole) was obtained *dimethyl* p-*trimethylsilylphenyl phosphate* (44%), b. p. 152—154°/4 mm., n_D^{20} 1·4862 (Found: C, 47·8; H, 6·9. $C_{11}H_{19}O_4PSi$ requires C, 48·1; H, 7·0%).

Thermal Decomposition.—When tristrimethylsilylmethylphosphine oxide was refluxed in a slow stream of nitrogen, with continuous removal of volatile material from the top of the condenser, the temperature of the boiling liquid fell from 270° to 220° during 3 hr., and a little liquid of b. p. 95—103°, n_D^{20} 1·3771, was collected. This gave silica on burning, and is believed to be hexamethyldisiloxane (b. p. 101°, n_D^{20} 1·3774).

When di-n-butyl trimethylsilylmethylphosphonate was boiled under similar conditions for 6 hr., a little liquid of b. p. 102—104°, n_D^{20} 1·387, was collected and the residue became dark brown. Some porous pot was added and the heating continued for 1 hr.; the residue was transformed into a brittle white solid insoluble in alcohol or hydrocarbons.

We thank Messrs. Albright and Wilson (Mfg.) Limited for the gift of several organophosphorus compounds.

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[*Received, June* 19*th*, 1959.]