178. *Preparation and Properties of 2-Chloroalkyl Esters of Boric, Silicic, and Phosphoric Acids.*

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Improved methods are described for the preparation of 2-chloroalkyl esters of ortho-boric, -silicic, and -phosphoric acids. The physical properties of these esters have been examined. Parachor measurements reveal that the values of the parachor constants of boron and silicon depend upon the molecular weight and complexity of the compound under investigation.

The first halogenoalkyl borate was prepared by Councler (*J. pr. Chem.*, 1878, **18**, 380), who obtained tri-2 : 3-dibromopropyl borate by the action of bromine on triallyl borate. In a study of the action of bleaching powder and boric acid on dimethylpentanol, Pastureau and Veiler (*Compt. rend.*, 1936, **202**, 1683) obtained the boric ester of the chlorohydrin of dimethylpentanol, which was also prepared by the action of boric acid on the chlorohydrin of tetramethylglycerol; the latter method was further used for the preparation of the boric esters of the chlorohydrins of trimethylethylglycerol and dimethyldiethylglycerol. Dupire (*ibid.*, p. 2086) prepared boric esters by refluxing mixtures of the appropriate alcohol, boric acid, and toluene, and removing water from the condensed vapours by means of anhydrous copper sulphate. By this method, which is claimed to avoid the formation of esters of metaboric acid, Dupire was able to prepare the boric ester of 1-chloro-2 : 3-dihydroxypropane. Through the interaction of chloral and triethylborine, Meerwein, Hinz, Majert, and Sönke (*J. pr. Chem.*, 1937, **147**, 226) prepared the trichloroethyl ester of diethylboric acid, while Meerwein, Hinz, Hofmann, Kroning, and Pfeil (*ibid.*, p. 257) obtained similar halogenated derivatives of boric esters by the action of boron trifluoride etherate upon epichlorohydrin.

Employing a modification of the method of Dupire (*loc. cit.*), we have prepared *tri-2-chloroethyl orthoborate*, $B(O\cdot CH_2\cdot CH_2Cl)_3$, and *tri-2 : 2′-dichloro*iso*propyl orthoborate*, $B[O\cdot CH(CH_2Cl)_2]_3$. These esters are colourless liquids with little odour, and the *iso*propyl derivative is highly viscous. Both liquids are readily hydrolysed by moisture with formation of the corresponding chlorohydrin and boric acid. Parachor measurements reveal that the parachor constants of boron in these esters are 21·6 and 37·1, respectively. Inasmuch as the parachor constants of this element in simple alkyl orthoborates (Sugden, " The Parachor and Valency," London, 1930, p. 187) range from 15·9 to 17·8, it appears that the observed value of the constant rises with increasing molecular weight and complexity of the boron compound.

The two chloroalkyl orthosilicates hitherto prepared are those of tetra-2-chloroethyl $Si(O\cdot CH_2\cdot CH_2Cl)_4$ and tetra-2-chloro*iso*propyl $Si[O\cdot CH(CH_2Cl)\cdot CH_3]_4$, which were obtained by Taurke (*Ber.*, 1905, **38**, 1667) by the action of silicon tetrachloride on the appropriate glycol or chlorohydrin. Dearing and Reid (*J. Amer. Chem. Soc.*, 1928, **50**, 3058) also prepared tetra-2-chloroethyl orthosilicate of 94% purity through interaction of silicon tetrachloride and ethylene chlorohydrin. We have prepared this ester in the pure state by the action of silicon tetrachloride on a benzene solution of ethylene chlorohydrin, and have further employed the modified method for the preparation of *tetra-2 : 2′-dichloro*iso*propyl orthosilicate* $Si[O\cdot CH(CH_2Cl)_2]_4$. These substituted alkyl orthosilicates are faintly sharp smelling, highly viscous liquids. Measurements of the parachor of these liquids show that the parachor constant of silicon in them is much higher than in the simpler compounds of this element. The change in the value of the constant with increasing molecular weight *M* and complexity of the compound is evident from Table I.

TABLE I.

Parachor constant of silicon.

	M.	[*P*].		*M.*	[*P*].
Silicon tetrachloride	169·9	25·0	Tetra-*n*-propylsilicane	200·4	30·9
Methyl orthosilicate	152·2	26·3	Tetraphenylsilicane	336·5	37·3
Ethyl orthosilicate	208·3	26·8	Tetra-2-chloroethyl orthosilicate	346·1	38·7
Tetraethylsilicane	144·3	31·6	Tetra-2 : 2′-dichloro*iso*propyl orthosilicate	540·0	32·6

Halogenoalkyl orthophosphates have been prepared by a variety of methods. Plimmer and Burch (*J.*, 1929, 284) obtained 3 c.c. of tri-2-chloroethyl orthophosphate, $PO(O\cdot CH_2\cdot CH_2Cl)_3$, by direct interaction of phosphorus oxychloride and ethylene chlorohydrin. The substance is reported to have b. p. 140°/40 mm. and *d* 1·39. We have prepared the compound in quantity by the controlled interaction of a benzene solution of phosphorus oxychloride and a pyridine–benzene solution of ethylene chlorohydrin. The compound so obtained is a colourless, fairly viscous liquid, b. p. 180°/5 mm., $d_{4°}^{20°}$ 1·4256, and analysis in conjunction with parachor measurements proved that the substance has the structure $O\leftarrow P(OCH_2\cdot CH_2Cl)_3$. *Tri-2 : 2′-dichloro*iso*propyl orthophosphate*, $O\leftarrow P[O\cdot CH(CH_2Cl)_2]_3$, was also prepared by the same method from glycerol dichlorohydrin. The viscosity of this ester was so high that its surface tension could not be measured by the Jaeger–Sugden method.

EXPERIMENTAL.

The substances and solvents used in the preparative work had all been carefully purified, and the liquids were redistilled with exclusion of moisture immediately before use.

Tri-2-chloroethyl Orthoborate.—The apparatus consisted of a 500-c.c. round-bottomed flask connected to a Soxhlet extractor, which was provided with a thermometer in the vapour space and with a reflux condenser. Boric anhydride (17·4 g.) and ethylene chlorohydrin (200 c.c.) were placed in the flask, and the Soxhlet thimble was charged with anhydrous copper sulphate (70—80 g.). A small cone of filter-paper, apex downward, was placed at the top of the thimble in order to direct the liquid condensate, falling from the condenser and the thermometer, to the centre of the copper sulphate, and thus ensure optimum conditions for the removal of water. The mixture in the flask was refluxed in an oil-bath kept at 170—180° for 2 hours during which period the temperature of the vapour in the Soxhlet enclosure rose to 120°. At this stage the thimble was replaced by another containing a similar quantity of anhydrous copper sulphate. The contents of the first thimble were filtered at the pump and the filtrate returned to the reaction vessel. The mixture was refluxed for a further 2—3 hours while the bath temperature was slowly raised to 200°.

The reaction mixture was transferred to a distillation apparatus, and the excess of chlorohydrin removed at a pressure of 200 mm. by distillation from an oil-bath at 190°. The residue was fractionated under reduced pressure in a Claisen unit; the pure *ester* had b. p. 117°/5 mm., 133°/10 mm., 143°/15 mm., 156°/25 mm., 175°/50 mm. Yield 90%. The material was analysed for C, H, and Cl by the usual methods, and boron was estimated by adding about 0·7 g. of the ester to 30—40 c.c. of carbon dioxide-free water, then 5 g. of mannitol, and titrating the solution with 0·1N-sodium hydroxide with phenolphthalein as indicator (Found : C, 28·7; H, 4·9; Cl, 43·1; B, 4·3. $C_6H_{12}Cl_3O_3B$ requires C, 28·9; H, 4·8; Cl, 42·7; B, 4·3%). The ester is a colourless liquid and has little odour. Like the simple trialkyl orthoborates, it undergoes rapid hydrolysis in a moist atmosphere, forming boric acid and ethylene chlorohydrin.

*Tri-2 : 2′-dichloro*iso*propyl Orthoborate.*—This was prepared from boric anhydride and glycerol *αα′*-dichlorohydrin with toluene as a solvent. This procedure avoided the use of a large excess of the chlorohydrin and enabled the eliminated water to be removed by distillation.

The apparatus consisted of a round-bottomed flask (500 c.c.) provided with a well-lagged eight-pear column in communication with a condenser. The flask was charged with boric anhydride (7 g.), the dichlorohydrin (66 c.c.), and toluene (200 c.c.), and the mixture was heated in an oil-bath. The temperature of distillation was allowed to rise to 115° during 90 minutes. The upper layer of the distillate was then separated from the aqueous layer and returned to the reaction flask. The process was repeated until the condensate was free from water. The excess of toluene was then distilled from the reaction mixture, and the residue fractionated in a Claisen apparatus. The pure borate was collected at 198°/5 mm.; at higher pressures the liquid boiled at 215°/10 mm., 227°/15 mm., and 240°/25 mm. (Found: C, 27·0; H, 3·7; Cl, 53·8; B, 2·7. $C_9H_{15}O_3Cl_6B$ requires C, 27·3; H, 3·8; Cl, 53·9; B, 2·7%). The ester resembles the lower homologue in its properties.

Tetra-2-chloroethyl Orthosilicate.—The reaction vessel consisted of a 1-l. distillation flask with its side tube bent upwards and connected to an inclined condenser, to the upper end of which was attached a downward-directed pipette. The latter passed through a stopper in a conical flask provided with a guard tube of calcium chloride. The distillation flask was provided with a stopper carrying a dropping funnel, and a gas-inlet tube reaching to the bottom of the flask. A solution of ethylene chlorohydrin (90 c.c.) in benzene (150 c.c.) was placed in the flask, and the end of the pipette immersed in ethylene chlorohydrin (10 c.c.) in the conical flask (cooled in a freezing mixture) in order to trap silicon tetrachloride vapour. A solution of silicon tetrachloride (38 c.c.) in benzene (100 c.c.) was added dropwise to the ethylene chlorohydrin solution, which was cooled in an ice–salt mixture, so that hydrogen chloride was quietly evolved during a period of 90 minutes. The freezing bath was then replaced by a water-bath, and the mixture slowly brought to the boil during 2 hours. At this stage the contents of the trap were transferred to the reaction flask, and the mixture was gently boiled for a further 2—3 hours while a stream of dry carbon dioxide was led through the solution to remove hydrogen chloride. The solvent was removed by distillation, and the residue fractionated in the usual manner. The pure ester had b. p. 174°/5 mm., 188°/10 mm., 205°/20 mm., 227°/50 mm. At atmospheric pressure the liquid boiled at 320° with slow decomposition. Yield 88%. It is a colourless, slightly viscous liquid with a slightly sharp odour. It undergoes little hydrolysis when treated with boiling water, but the hydrolysis is rapid in boiling alkali solution.

*Tetra-2 : 2′-dichloro*iso*propyl Orthosilicate.*—This ester was prepared by refluxing a mixture of glycerol αα′-dichlorohydrin (60 c.c.), silicon tetrachloride (19 c.c.), and benzene (250 c.c.) for 8 hours in a stream of dry carbon dioxide to effect complete removal of hydrogen chloride. The solvent was removed by distillation, and the residue fractionated under reduced pressure. The pure *silicate* distilled at 244°/5 mm., 253°/10 mm., and 259°/15 mm. Yield 90% (Found: C, 26·8; H, 3·8; Cl, 51·5; Si, 5·2. $C_{12}H_{20}O_4Cl_8Si$ requires C, 26·7; H, 3·7; Cl, 52·5; Si, 5·2%). For the silicon determination a small weight of the ester was carefully treated directly with a mixture of sulphuric and fuming nitric acids in a covered crucible, then warmed, and finally ignited to silica. The freshly distilled ester is a colourless, highly viscous liquid, which, on standing for several hours, becomes pink. This is probably due to the separation of silica in highly disperse condition. The ester is insoluble in water, but is hydrolysed by boiling sodium hydroxide solution.

Tri-2-chloroethyl Orthophosphate.—The apparatus for the preparation of this substance consisted of a 1-l. flask provided with a dropping funnel, a mercury-sealed stirrer, and an exit tube fitted with a guard tube of calcium chloride. To a well-cooled, thoroughly stirred mixture of ethylene chlorohydrin (100 c.c.), pyridine (120 c.c.), and benzene (300 c.c.) was added dropwise a solution of phosphorus oxychloride (46 c.c.) in benzene (100 c.c.) during 90 minutes. Stirring was continued for a further 3 hours, and the mixture was then set aside for 24 hours. The pyridine hydrochloride was filtered off at the pump, and washed with benzene (60 c.c.). The benzene was removed from the reaction mixture by distillation, the residue washed with water, and then dried before being subjected to fractionation. The ester boiled at 180°/5 mm., 194°/10 mm., 202°/15 mm., 214°/25 mm. In view of the great discrepancy between our values and those given by Plimmer and Burch (*loc. cit.*) for the b. p. and density, our material was subjected to analysis. Chlorine was estimated by the Carius procedure. For the phosphorus determination, on the advice of Dr. D. T. Lewis, we heated a small weight of the ester with concentrated sulphuric and fuming nitric acids in a Kjeldahl flask until clear, neutralised the mixture with ammonia, then acidified it with acetic acid, and treated it in boiling solution with slight excess of uranyl acetate and ammonium acetate; the precipitate was ignited to uranyl pyrophosphate, which was weighed (Found: C, 25·2; H, 4·7; Cl, 37·5; P, 11·2. $C_6H_{12}O_4Cl_3P$ requires C, 25·1; H, 4·2; Cl, 37·3; P, 10·9%). Further confirmation of the structure of the compound is furnished by the parachor measurements described below. The *ester* is a colourless, fairly viscous liquid with a faint buttery smell. It is not appreciably hydrolysed by boiling water and only slightly by sodium hydroxide solution.

*Tri-2 : 2′-dichloro*iso*propyl Orthophosphate.*—This ester was prepared by stirring a well-cooled mixture of glycerol αα′-dichlorohydrin (60 c.c.), pyridine (48 c.c.), and benzene (150 c.c.) with a solution of phosphorus oxychloride (18 c.c.) in benzene (100 c.c.) in accordance with the previously described procedure. After separation of the pyridine hydrochloride, the benzene was distilled from the solution, and the residue was washed with sodium hydroxide solution and then dried before fractionation. The *ester* was collected at 236—237°/5 mm.; it also boiled at 246°/10 mm. and 252°/15 mm. Yield 50% (Found: C, 24·8; H, 3·7; Cl, 49·4; P, 7·6. $C_9H_{15}O_4Cl_6P$ requires C, 25·0; H, 3·5; Cl, 49·4; P, 7·3%). It is not hydrolysed by water or to any appreciable extent by sodium hydroxide solution.

All the esters described above are miscible with alcohol, ether, or benzene.

Boiling Points and Densities.—These physical constants were determined in the manner described by Evans, Davies, and Jones (*J.*, 1930, 1311); the densities, $d_{4^\circ}^{20^\circ}$, in g. per c.c., are recorded in Table II. The following equations give for each ester the b.p., t° c., under a pressure p mm. of mercury.

$$\begin{array}{ll}
B(O\cdot CH_2\cdot CH_2Cl)_3 & \log_{10} p = 8\cdot 4144 - 3012/(t + 273\cdot 2) \\
B[O\cdot CH(CH_2Cl)_2]_3 & \log_{10} p = 9\cdot 2584 - 4032/(t + 273\cdot 2) \\
Si(O\cdot CH_2\cdot CH_2Cl)_4 & \log_{10} p = 10\cdot 1634 - 4237/(t + 273\cdot 2) \\
Si[O\cdot CH(CH_2Cl)_2]_4 & \log_{10} p = 18\cdot 1127 - 9009/(t + 273\cdot 2) \\
PO(O\cdot CH_2\cdot CH_2Cl)_3 & \log_{10} p = 10\cdot 6449 - 4505/(t + 273\cdot 2) \\
PO[O\cdot CH(CH_2Cl)_2]_3 & \log_{10} p = 16\cdot 5224 - 8065/(t + 273\cdot 2)
\end{array}$$

Refractive Indices.—These were determined as described by Jones, Davies, and Dyke (*J. Physical Chem.*, 1933, **37**, 583), and the values are recorded in Table II.

TABLE II.

Substance.	$d_{4^\circ}^{20^\circ}$.	$n_F^{20^\circ}$.	$n_D^{20^\circ}$.	$n_C^{20^\circ}$.
$B(O\cdot CH_2\cdot CH_2Cl)_3$	1·2780	1·4611	1·4556	1·4533
$B[O\cdot CH(CH_2Cl)_2]_3$	1·4028	1·4945	1·4883	1·4858
$Si(O\cdot CH_2\cdot CH_2Cl)_4$	1·3393	1·4699	1·4641	1·4617
$Si[O\cdot CH(CH_2Cl)_2]_4$	1·4538	1·5030	1·4968	1·4942
$PO(O\cdot CH_2\cdot CH_2Cl)_3$	1·4256	1·4786	1·4731	1·4708
$PO[O\cdot CH(CH_2Cl)_2]_3$	1·5182	1·5083	1·5022	1·4997

Viscosities.—The viscometers employed were of the Ostwald type modified to conform with the specifications of B.S.S. viscometers and the recommendations of Barr (" Monograph of Viscometry," Oxford, 1931). Owing to the wide range of viscosities exhibited by the esters, it was necessary to use three different instruments in order to obtain reasonable times of flow. Water could not be employed as calibrating liquid owing to the disparity between its viscosity and that of the esters under investigation. Accordingly, sucrose solutions (concentration 40% and 60%) were used as calibrating liquids. These solutions were prepared from " AnalaR " sucrose and were filtered through a sintered-glass filter before use. The density and viscosity values given in the International Critical Tables were used in the calculations.

The viscometers were adequately protected by means of guard tubes of calcium chloride, and the instruments were charged with a known volume of the ester under conditions which prevented the intrusion of moisture. Plugs of cotton-wool were arranged to prevent passage of dust particles into the apparatus. The measurements were carried out in a thermostat at 20° ± 0·02°, and the times of flow were observed by means of a stop-watch which had been calibrated against a standard chronometer. All measurements were conducted with due observance of the customary precautions.

Surface Tensions.—These were measured by the Jaeger–Sugden method in the apparatus described by Bowden and Butler (*J.*, 1939, 83). The apparatus was calibrated in the usual way with benzene, and the esters were freshly distilled immediately before use.

The results are collected in Table III, where η is the viscosity in centipoises, γ is the surface tension in dynes per cm., and $[P]$ the parachor.

TABLE III.

Substance.	$\eta^{20°}$.	$\gamma^{20°}$.	$[P]_{\text{obs.}}$.	$[P]_{\text{calc.}}$.
$B(O{\cdot}CH_2{\cdot}CH_2Cl)_3$	6·871	39·19	488·5	473·3
$B[O{\cdot}CH(CH_2Cl)_2]_3$	287·1	43·40	722·6	701·9
$Si(O{\cdot}CH_2{\cdot}CH_2Cl)_4$	9·830	39·56	647·9	634·2
$Si[O{\cdot}CH(CH_2Cl)_2]_4$	579·6	42·28	946·6	940·0
$PO(O{\cdot}CH_2{\cdot}CH_2Cl)_3$	42·90	43·83	515·2	513·0
$PO[O{\cdot}CH(CH_2Cl)_2]_3$	2901	—	—	—

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