376. *Structural Chemistry of the Alkoxides. Part I. Amyloxides of Silicon, Titanium, and Zirconium.*

By D. C. Bradley, R. C. Mehrotra, and W. Wardlaw.

The isomeric amyloxides $M(OC_5H_{11})_4$ of titanium and zirconium have been prepared by alcoholysis. Boiling points (under reduced pressure) and molecular weights of these compounds and of *n*-amyl and *neo*pentyl orthosilicates have been measured. The influence of branching of the amyl group on the physical properties of these compounds is discussed.

Although the preparation of the tetramethoxide and tetraethoxide of zirconium was reported as far back as 1929 (Meerwein and Bersin, *Annalen,* **476**, 113) it was not until 1951 that the remarkable influence of the nature of the alkyl group on the physical properties of the zirconium alkoxides was discovered (Bradley and Wardlaw, *J.*, 1951, 280). It was then shown that the outstanding feature of zirconium alkoxides was the increased volatility as the alkyl group was changed from primary to secondary to tertiary. A survey of the literature revealed that a similar phenomenon occurred with the alkoxides of silicon and titanium but to a smaller degree.

We are now making a detailed study of the relations between structure and physical properties amongst the alkoxides of Group IV elements and related elements. The results now presented lend strong support to the theory proposed in our earlier paper (*loc. cit.*). It was suggested that intermolecular bonding of unusual strength might be responsible for the low volatility of the primary alkoxides, whilst branching of the alkyl group prevents this association. To test the validity of this the isomeric amyloxides of silicon, titanium, and zirconium were studied. This series was selected because the molecular weight of alkyl group remained constant and particularly because little was known about the properties of these compounds.

The new alkoxides were prepared from the *iso*propoxides by the following reactions :

$$\mathrm{Ti(OPr^i)_4 + 4C_5H_{11}{\cdot}OH \longrightarrow Ti(OC_5H_{11})_4 + 4Pr^i{\cdot}OH}$$
$$\mathrm{Zr(OPr^i)_4,Pr^i{\cdot}OH + 4C_5H_{11}{\cdot}OH \longrightarrow Zr(OC_5H_{11})_4 + 5Pr^i{\cdot}OH}$$

Provided certain precautions are taken, quantitative yields of the required alkoxides can be obtained when using the minimum amount of amyl alcohol.

The following table summarises our results :

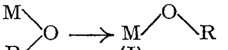
	Titanium alkoxide			Zirconium alkoxide		
Alcohol	B. p./mm.	*M*	Molecular complexity	B. p./mm.	*M*	Molecular complexity
$\mathrm{CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$	175°/0·8	565	1·4	256°/0·01	1428	3·2
$\mathrm{CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$	148°/0·1	490	1·2	247°/0·1	1462	3·3
$\mathrm{CHMeEt{\cdot}CH_2{\cdot}OH}$	154°/0·5	422	1·1	238°/0·1	1615	3·7
$\mathrm{CMe_3{\cdot}CH_2{\cdot}OH}$	105°/0·05	500	1·3	188°/0·2	1051	2·4
$\mathrm{CHEt_2{\cdot}OH}$	112°/0·05	399	1·0	178°/0·05	868	2·0
$\mathrm{CHMePr^nOH}$	135°/1·0	410	1·0	175°/0·05	860	2·0
$\mathrm{CHMePr^i{\cdot}OH}$	131°/0·5	415	1·0	156°/0·01	870	2·0
$\mathrm{CMe_2Et{\cdot}OH}$	98°/0·1	405	1·0	95°/0·1	455	1·0

In addition we found that the *n*-amyloxide of silicon (b. p. 134°/0·1 mm.), although monomeric, was much less volatile than the isomeric *neo*pentyl orthosilicate (b. p. 85°/0·1 mm.).

The striking change in volatility of the amyloxides is seen more effectively in Fig. 1, where the boiling points at 0·1 mm. are compared.

The important points which emerge from our detailed study of these amyloxides are as follows. Branching of the amyl groups leads to increased volatility in the alkoxides of silicon, titanium, and zirconium but the effect is most pronounced with the zirconium derivatives. Further it is established that volatility is directly related to molecular complexity (determined ebullioscopically in benzene) in the amyloxides of zirconium. Although less pronounced, a similar trend in molecular complexity occurs with the titanium derivatives, but there is little doubt that all the amyloxides of silicon are monomeric.

It seems reasonable to suppose that intermolecular bonding accounts for the abnormally high boiling points of the less branched compounds and involves the mechanism (I). This type of molecular association will be strongly opposed when the central atom is shielded by branched alkoxide groups. In the monomeric amyloxides it is evident that the shielding is complete.


(I)

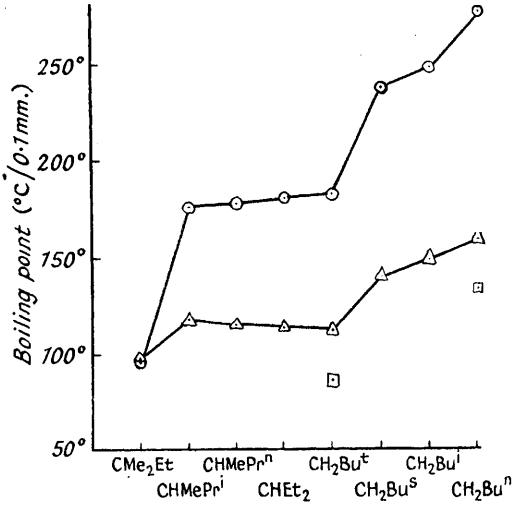
The contrast between the properties of the alkoxides of zirconium on the one hand and those of titanium and silicon on the other, invites some comment. It may well be that this behaviour is connected with the atomic radius of the central atom. Thus zirconium will require more effective shielding than the smaller silicon or titanium. It is noteworthy that in combination with oxygen the maximum covalency of silicon and of titanium is 6 whereas zirconium can exhibit a covalency of 8.

The alternative possibility cannot be ignored that the abnormal behaviour of zirconium is due to the intermolecular bonding O→M being stronger for zirconium than for silicon or titanium, and as a consequence the complex structure of zirconium alkoxides may persist in the vapour phase. This view is supported by the linear relation between molecular complexity and boiling point for the amyloxides of zirconium (Fig. 2; for fractional values of molecular complexity the lower integer is taken, *e.g.*, 3·3 becomes 3). The possibility that complex molecules exist in the vapour is being investigated experimentally.

In our earlier communication (*loc. cit.*) it was observed that the influence of chain branching on volatility might arise from the (+*I*) effect of the alkyl group. For example, the structure $\mathrm{R{-}\overset{+}{O}{=}\overset{-}{Zr}}$ would be stabilised by the (+*I*) effect of the group R, and it is known that the (+*I*) effect increases in the order primary<secondary<tertiary. Although this

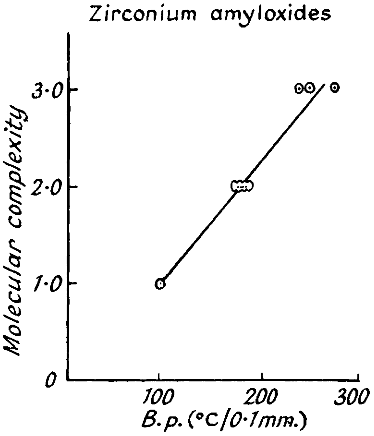
" intramolecular " bonding may be present in tertiary alkoxides there is evidence which supports the view that steric effects predominate in determining the volatility and complexity of the alkoxides. In Figs. 1 and 2 it is clear that the *neo*pentyloxide behaves as though it were a " secondary " amyloxide. Since the $(+I)$ effects of the primary amyl groups are similar in magnitude, it is concluded that the abrupt change in physical properties must arise from the enhanced steric effect of the *neo*pentyl group.

FIG. 1.



R *group in* $M(OR)_4$: ⊙ Zr; △Ti; ⊡ Si.

FIG. 2.



EXPERIMENTAL

Apparatus.—All-glass apparatus fitted with standard interchangeable joints was used and special precautions were taken to exclude moisture. In the alcoholysis experiments fractionations were carried out by using a column (60 cm.) packed with Fenske helices and fitted to a total-condensation variable take-off stillhead.

Reagents.—With the following exceptions, the alcohols were commercial products of reagent grade. 1-Methylbutanol and 1 : 2-dimethylpropanol were prepared from acetaldehyde and the appropriate Grignard reagents. *neo*Pentyl alcohol was prepared by Conant, Webb, and Mendin's method (*J. Amer. Chem. Soc.*, 1929, **51**, 1246). Each alcohol was finally purified by fractionation in the apparatus described above.

Titanium *iso*propoxide was prepared by R. Gaze's method (to be published), which involved treatment of a solution of titanium tetrachloride and *iso*propanol in benzene with ammonia. The final product was distilled at 80°/2·0 mm. (yield 72%) [Found : Ti, 16·9; Pr^iO, 82·9. Calc. for $Ti(OC_3H_7)_4$: Ti, 16·85; Pr^iO, 83·15%].

Zirconium *iso*propoxide was prepared from the tetrachloride by a modification of the original method (*loc. cit.*). Benzene was employed as solvent and only about 20% excess over the theoretical amount of *iso*propanol was added. Thus the initial reaction between zirconium tetrachloride and *iso*propanol was moderated and the removal of ammonium chloride could be completed in a single operation. After four recrystallisations from *iso*propanol, pure zirconium *iso*propoxide (66%) was obtained [Found : Zr, 23·55; Pr^iO, 76·2. Calc. for $Zr(OPr^i)_4,Pr^iOH$: Zr, 23·5 ; Pr^iO, 76·2%].

Analytical Methods.—Titanium and zirconium were determined gravimetrically as the oxides. *iso*Propoxide was determined volumetrically as previously described (*loc. cit.*). Carbon and hydrogen analyses were carried out by Messrs. Weiler and Strauss (Oxford), to whom we express our thanks for their co-operation in dealing with these difficult substances.

Molecular Weights.—A conventional pattern Menzies–Wright ebulliometer was fitted with a side cone (B. 19) for rapid introduction of samples. Above the condenser was fitted a socket (B. 24) for fixing either a still-head or the differential water-thermometer. Liquid samples were delivered from an all-glass weight pipette. " AnalaR " Benzene (sodium-dried) was fractionated with a 90-cm. column packed with Fenske helices.

In an experiment about 38 c.c. of benzene were collected in the clean dried apparatus and then distilled until a convenient volume (at the b. p. *ca.* 35 c.c.) remained. The whole apparatus was surrounded by a tubular draught shield. After the usual preliminary measurements, successive additions of solute were made, and each elevation recorded was the mean of five or six separate readings. In most cases freshly distilled samples of alkoxide were taken and the best linearity of elevation (ΔT) against weight of solute (m) was found with the monomeric substances.

The apparatus constant (per 100 c.c. of solvent) was determined by using azobenzene (31·49) and benzil (31·47).

The results are collected in the table.

Ebullioscopic Results.

Alkoxide	No. of detmtns.	Range of m, g.	Benzene, c.c.	$\Delta T/m$	M, found	M, calc.
$Ti(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me)_4$	5	0·167—1·116	36·2	0·154°	565	396·5
$Ti(O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2)_4$	3	0·130—0·693	35·0	0·184	490	,,
$Ti(O{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2Me)_4$	5	0·089—0·866	35·0	0·213	422·5	,,
$Ti(O{\cdot}CH_2{\cdot}CMe_3)_4$	4	0·163—0·545	36·7	0·172	500	,,
$Ti(O{\cdot}CHEt_2)_4$	4	0·165—1·018	34·95	0·226	399	,,
$Ti(O{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Me)_4$	5	0·209—1·143	35·9	0·214	410	,,
$Ti(O{\cdot}CHMe{\cdot}CHMe_2)_4$	6	0·196—0·974	34·9	0·218	415	,,
$Ti(O{\cdot}CMe_2{\cdot}CH_2Me)_4$	5	0·222—1·357	34·0	0·229	404	,,
$Zr(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me)_4$	6	0·567—1·785	35·7	0·0618	1428	439·8
$Zr(O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2)_4$	5	0·152—0·997	35·9	0·060	1462	,,
$Zr(O{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2Me)_4$	4	0·188—0·983	35·6	0·0548	1615	,,
$Zr(O{\cdot}CH_2{\cdot}CMe_3)_4$	5	0·344—1·698	36·75	0·0815	1051	,,
$Zr(O{\cdot}CHEt_2)_4$	4	0·200—0·936	34·9	0·104	868	,,
$Zr(O{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Me)_4$	3	0·213—0·886	35·9	0·102	860	,,
$Zr(O{\cdot}CHMe{\cdot}CHMe_2)_4$	6	0·215—1·427	35·5	0·102	870	,,
$Zr(O{\cdot}CMe_2{\cdot}CH_2Me)_4$	4	0·555—2·037	35·9	0·193	454·5	,,
$Si(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me)_4$	5	0·327—1·230	34·3	0·252	364·4	376·6

Boiling Points.—Owing to the low volatility of most of the alkoxides, distillations had to be carried out at low pressures. Considerable efforts were made to standardise conditions, and the results are suitable for a preliminary comparative survey. The same semimicro-fractionation apparatus, fitted with a capillary leak and a " pig " for collecting three fractions, was used throughout, together with a Vacustat reading from 10·0 to 0·01 mm. In doubtful cases the product was redistilled until the b. p. remained constant within 0·2°. In some cases the b. p. at 0·1 mm. pressure had to be calculated from data at different pressures. Within the range 1·0—0·01 mm. pressure the following relations were assumed to hold :

P_1/P_2	10	5	2
$T_1 - T_2$	20°	14°	6°

These figures are based on experiments on different alkoxides and it is believed that the corrected results are reliable to within ±5°. Accurate vapour-pressure measurements are being carried out and will be reported later.

Alcoholysis Experiments.—The same technique for preparing titanium or zirconium alkoxides by alcoholysis was used throughout and detailed descriptions will be given only in two examples. By conducting the reactions in benzene the minimum quantity of alcohol was used. This is important for two reasons. First, some of the alcohols are expensive or inaccessible, and, secondly, side reactions are avoided especially with tertiary alcohols. Moreover, the *iso*propanol liberated in the reaction is readily removed by fractionation as the azeotrope with benzene, so the extent and speed of the reaction are easily observed. In general, the rates of alcoholysis for the titanium alkoxides were greater than the rates for the corresponding zirconium alkoxides.

*Titanium Tetra-*n*-pentyloxide.*—Titanium *iso*propoxide (6·4 g.) in benzene (60 c.c.) was caused to react with *n*-pentanol (9·1 g., b. p. 136°/750 mm.) at 130—140° under the fractionation column. During 1 hour's fractionation about 20 c.c. of azeotrope (b. p. 71—72°) were collected, followed by 10 c.c. of benzene. The remainder of solvent was evaporated off under reduced pressure, and the titanium amyloxide distilled at 175°/0·8 mm. (158°/0·1 mm.) and collected as a colourless liquid (8·4 g.) [Found: Ti, 12·16. Calc. for $Ti(OC_5H_{11})_4$: Ti, 12·09%]. Cullinane, Chard, Price, Millward, and Langlois (*J. Appl. Chem.*, 1951, **1**, 400) found b. p. 211°/11 mm., 314°/760 mm , and *M* (cryoscopic in benzene) 980.

Zirconium Tetra-n-*pentyloxide*.—Zirconium *iso*propoxide (5·7 g.) in benzene (60 c.c.) was treated at 130—140° with *n*-pentanol (10·7 g.), and 12 c.c. of azeotrope were collected in 2 hours. The b. p. of distillate (reflux ratio $>20 : 1$) then rose steadily from 72° to 80°, a clear indication of a slow alcoholysis reaction. About 30 c.c. of distillate, b. p. 80°, were collected, and the remainder of solvent was removed under reduced pressure. The final product was distilled at 256°/0·01 mm. (276°/0·1 mm.) and the colourless viscous distillate (6·2 g.) soon became coloured in contact with dry air [Found : Zr, 20·83. Calc. for $Zr(OC_5H_{11})_4$: Zr, 20·75%].

Titanium Tetra-3-*methylbutoxide*).—Titanium *iso*propoxide (8·5 g.) and 3-methylbutanol (15·5 g.; b. p. 129·8°/750 mm.) in benzene (70 c.c.) were caused to react as described above. The alkoxide (11·5 g., b. p. 148°/0·1 mm.) set to a colourless glass at room temperature [Found : Ti, 12·07. Calc. for $Ti(OC_5H_{11})_4$: Ti, 12·09%]. At higher solute concentrations than are given in the table the degree of association was higher : *e.g.*, $m = 0{\cdot}919$, $M = 531$; $m = 1{\cdot}069$, $M = 542$. Cullinane *et al.* (*loc. cit.*) found b. p. 214°/25 mm., *M* (cryoscopic), 553—857.

Zirconium Tetra-(3-*methylbutoxide*).—Zirconium *iso*propoxide (6·3 g.) in benzene (70 c.c.) was treated with 3-methylbutanol (9·2 g.) in the usual way. The new *alkoxide* was a colourless glassy solid (7·0 g., b. p. 247°/0·1 mm.) [Found : Zr, 21·05; C, 53·4; H, 9·8. $Zr(OC_5H_{11})_4$ requires Zr, 20·75; C, 54·6; H, 10·1%].

Titanium Tetra-(2-*methylbutoxide*).—Titanium *iso*propoxide (5·5 g.) and 2-methylbutanol (10·4 g., b. p. 128°/755 mm.) reacted together in benzene (60 c.c.) as before. After distillation at 154°/0·5 mm. (140°/0·1 mm.), the final product was a colourless solid (7·6 g.) (Found : Ti, 12·14%).

Zirconium Tetra-(2-*methylbutoxide*).—Zirconium *iso*propoxide (5·0 g.) in benzene (60 c.c.) was treated with 2-methylbutanol (8·7 g.), and the new *alkoxide* distilled at 238°/0·1 mm. The colourless liquid distillate set to a glassy solid (5·5 g.) (Found : Zr, 20·95%). The value of *M* (table) may be high owing to ageing (3 days) of the sample before the determination was carried out.

*Titanium Tetra*neo*pentyloxide*.—Titanium *iso*propoxide (3·5 g.) and *neo*pentyl alcohol (5·1 g., b. p. 113·5°/755 mm.) were caused to react in benzene (28·8 g.) at 130°, and the azeotrope was collected. The solution was concentrated to 10 c.c. and then deposited crystals which were separated and dried at room temperature (0·5 mm. pressure) for 6 hours [Found : Ti, 12·20; C, 58·6; H, 10·9. $Ti(OC_5H_{11})_4$ requires Ti, 12·09; C, 60·6; H, 11·2%]. The mother-liquor was dried under reduced pressure to a white solid which melted at *ca.* 70° (bath temp.), the liquid distilling at 105°/0·05 mm. (111°/0·1 mm.). The white crystalline distillate of the *alkoxide* melted sharply at 64° (Found : Ti, 12·24%).

*Zirconium Tetra*neo*pentyloxide*.—The alcoholysis reaction of zirconium *iso*propoxide (8·0 g.) with *neo*pentyl alcohol (8·8 g.) in benzene (50 c.c.) required 3 hours at 130° for completion. Solvent was evaporated at reduced pressure and a white solid was deposited. This melted between 150° and 160° (bath temp.) and distilled at 176°/0·05 mm. or 188°/0·2 mm. (182°/0·1 mm.) The distillate, a white crystalline mass of the *alkoxide* (8·6 g.), melted between 154° and 157° (Found : Zr, 21·01; C, 52·8; H, 9·8%].

Titanium Tetra-(1-*ethylpropoxide*).—Titanium *iso*propoxide (11·1 g.) in benzene (70 c.c.) reacted with 1-ethylpropanol (16·5 g.; b. p. 115·4°/755 mm.) and the new titanium *alkoxide* distilled at 112°/0·1 mm. The distillate, a colourless mobile liquid (15·2 g.), was only slowly hydrolysed in moist air [Found : Ti, 12·12; C, 59·0; H, 11·0%].

Zirconium Tetra-(1-*ethylpropoxide*).—Zirconium *iso*propoxide (9·2 g.) in benzene (80 c.c.) reacted with 1-ethylpropanol (11·6 g.). The new zirconium *alkoxide* distilled at 178°/0·08 mm. (181°/0·1 mm.) and gave a colourless glassy solid (10·4 g.) (Found : Zr, 20·80%).

Titanium Tetra-(1-*methylbutoxide*).—The alcoholysis of titanium *iso*propoxide (6·2 g.) with 1-methylbutanol (13·4 g.; b. p. 118·5°/750 mm.) in benzene (60 c.c.) afforded a colourless mobile liquid (8·2 g.) which was distilled at 135°/1·0 mm. (115°/0·1 mm.) [Found : Ti, 12·12; C, 57·8; H, 11·0%].

Zirconium Tetra-(1-*methylbutoxide*).—Zirconium *iso*propoxide (4·7 g.) reacted in benzene (40 c.c.) with 1-methylbutanol (8·8 g.) in the usual way. The final product was distilled at 175°/0·08 mm. (178°/0·1 mm.) and gave a colourless viscous liquid (5·0 g.) (Found : Zr, 20·85%).

Titanium Tetra-(1 : 2-*dimethylpropoxide*).—Titanium *iso*propoxide (6·5 g.) in benzene (70 c.c.) reacted with 1 : 2-dimethylpropanol (11·0 g.; b. p. 111°/753 mm.) to give the titanium *alkoxide*, which distilled at 131°/0·5 mm. (117°/0·1 mm.) and gave a colourless mobile liquid (5·0 g.) (Found : Ti, 12·12%).

Zirconium Tetra-(1 : 2-*dimethylpropoxide*).—Zirconium *iso*propoxide (8·0 g.) and 1 : 2-dimethylpropanol (10·3 g.) in benzene (70 c.c.) afforded the new *alkoxide*; after distillation at 156°/0·01 mm. (176°/0·1 mm.), this set to a colourless opaque solid (8·3 g.) (Found : Zr, 21·13%).

Titanium Tetra-(1 : 1-*dimethylpropoxide*).—From the alcoholysis reaction between titanium *iso*propoxide (8·4 g.) and 1 : 1-dimethylpropanol (13·0 g.; b. p. 101·4°/740 mm.) in benzene (80 c.c.) a colourless mobile liquid (11·6 g., b. p. 98°/0·1 mm.) was isolated (Found : Ti, 12·08%). (This compound was first prepared by D. C. Hancock, Thesis, London Univ., 1952.)

Zirconium Tetra-(1 : 1-*dimethylpropoxide*).—1 : 1-Dimethylpropanol (16·0 g.) and zirconium *iso*propoxide (12·4 g.) in benzene (75 c.c.) afforded the new *alkoxide* as a colourless mobile liquid (13·7 g.), b. p. 95°/0·1 mm., 121°/2·0 mm., which slowly discoloured in dry air [Found : Zr, 20·75; C, 53·85; H, 10·4%].

n-*Amyl Orthosilicate.*—*n*-Amyl alcohol (28·5 g.) was added dropwise to silicon tetrachloride (13·2 g.) and a vigorous reaction took place with evolution of hydrogen chloride. Removal of this gas was completed by aspiration with dry nitrogen (2 hours) and the final product distilled at 143°/0·3 mm. The pale brown distillate was redistilled (134°/0·1 mm.) and gave a colourless product (20 g.) [Found : Si, 7·48. Calc. for $Si(OC_5H_{11})_4$: Si, 7·45%]. Ridge and Todd (*J.*, 1949, 2637) found b. p. 302—304°/760 mm.

neo*Pentyl Orthosilicate.*—A preliminary experiment showed that *neo*pentyl alcohol reacted with silicon tetrachloride in light petroleum to give a white gelatinous precipitate. Accordingly, the reaction was conducted in the presence of pyridine. Silicon tetrachloride (4·4 g.) was added dropwise to a solution of *neo*pentyl alcohol (10 g.) and pyridine (11·7 g.; " AnalaR," dried over barium oxide) in light petroleum (40 c.c.). Next morning, the pyridine hydrochloride was separated and from the filtrate a colourless solid (6 g.) was isolated which was distilled (b. p. 85°/0·1 mm.; 94°/0·3 mm.). The neo*pentyl orthosilicate* set to a white crystalline solid which softened at 70° and melted at 75—76° (Found : Si, 7·51%).

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BIRKBECK COLLEGE, LONDON, W.C.1.

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