

## Alkali-metal Alkylberyllium Alkoxides

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Three series of alkali-metal t-butoxyberyllate complexes are described, including  $MBe(OBu^t)_3$  ( $M = Li, Na, K, Rb,$  or  $Cs$ ),  $[MEtBe(OBu^t)_2]_2$  ( $M = Li$  or  $Na$ ), and  $[MEt_2Be(OBu^t)]_2$  ( $M = Na$  or  $K$ ). The series  $MBe(OBu^t)_3$  is formed from  $MOBu^t$  and  $Be(OBu^t)_2$ , from  $Na_2BeH_4$  and  $Bu^tOH$ , or from  $K$  and  $Be(OBu^t)_2$  in  $Bu^tOH$ . The  $Li$  and  $Rb$  complexes crystallise from benzene though the others are insoluble in that solvent. The  $Li$  and  $Na$  complexes dissolve in bis(2-methoxyethyl) ether yielding hexane-soluble 1:1 monomeric co-ordination complexes. The  $LiBe(OSiMe_3)_3$  and  $LiBe(OBu^t)_2(OC_2H_5)_2$  complexes are dimeric in benzene solution. In contrast,  $LiBe(OC_2H_5)_3$  exists in a dimer-monomer equilibrium in benzene solution. The series  $[MEtBe(OBu^t)_2]_2$  are conveniently prepared from  $EtLi$  and  $Be(OBu^t)_2$  or from  $NaOBu^t$  and  $EtBeOBu^t$ . Replacement of the ethyl group in the former with a t-butyl group yields dimeric  $[LiBu^t(OBu^t)_2]_2$ , though  $Li_2Bu^t_2Be(OBu^t)_2$  has a degree of association of between 1 and 2 in benzene solution. Complexes of the type  $[MEt_2Be(OBu^t)]_2$  are readily prepared from equimolar mixtures of  $NaOBu^t$  or  $KOBu^t$  with  $Et_2Be$ , though  $Rb_2Et_3Be_2(OBu^t)_3$  is isolated from equimolar portions of  $RbOBu^t$  and  $Et_2Be$ . Sodium diethyl t-butoxyberyllate reacts with toluene or mesitylene giving red  $K_5Et_3Be_3(OBu^t)_4(PhCH_2)_4$  or orange diamagnetic  $K_3Et_2Be_2(OBu^t)_2(mesityl)_2$ , respectively. The rubidium complex gives red  $Rb_5Et_3Be_3(OBu^t)_2(mesityl)_4$  on reaction with mesitylene. Sparingly benzene-soluble  $LiBu^tBe(NMe_2)_2$  is also described.

In contrast to the several studies on alkali-metal dialkylberyllium hydride complexes<sup>1,2</sup> only scattered reports about alkali-metal beryllium alkoxides have appeared. Benzene-insoluble lithium tri-isopropoxyberyllate is

<sup>1</sup> N. A. Bell and G. E. Coates, *Proc. Chem. Soc.*, 1964, 59; *J. Chem. Soc.*, 1965, 692.

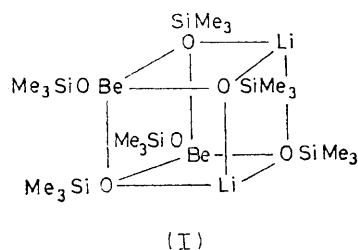
dimeric though its sodium analogue  $NaBe(OPr^i)_3$  is monomeric in refluxing isopropyl alcohol.<sup>3</sup> Sodium trimethoxyberyllate is insoluble in benzene and diethyl

<sup>2</sup> G. E. Coates and R. E. Pendlebury, *J. Chem. Soc. (A)*, 1970, 156.

<sup>3</sup> M. Arora and R. C. Mehrotra, *Indian J. Chem.*, 1969, 7, 399.

ether, though it dissolves in methanol yielding crystalline  $\text{NaBe}(\text{OMe})_3 \cdot \text{MeOH}$ . The complex has an appreciable dissociation pressure of methanol (3 mmHg at  $40^\circ$ ) which can be removed on exposure to vacuum.<sup>4</sup> These properties are consistent with the solvent-free complex having a polymeric constitution, as would result from every beryllium atom having a co-ordination number of four. The complex  $\text{K}_2\text{Be}(\text{OEt})_4$ <sup>5</sup> doubtless has a salt-like constitution similar to that found crystallographically for  $\text{Li}_2\text{Me}_4\text{Be}$ .<sup>6</sup> We now find that some alkali-metal beryllium alkoxides are volatile and rather soluble in hydrocarbon solvents.

Lithium tri-*t*-butoxyberyllate, prepared from lithium *t*-butoxide and beryllium di-*t*-butoxide, crystallises from benzene though it is not sufficiently soluble in that solvent to determine its molecular weight by methods currently available to us. Its sparing solubility suggests an oligomeric rather than a polymeric constitution. Since symmetry has a large effect on solubility properties, we replaced one methyl group by an ethyl group and obtained the benzene-soluble dimer  $[\text{LiBe}(\text{OBu}^t)_2(\text{OCMe}_2\text{Et})_2]$  which sublimes in vacuum at  $75\text{--}80^\circ$ . Lithium tri(2-methylbutoxy)beryllate,  $[\text{LiBe}(\text{OCMe}_2)_3]_2$ , is also dimeric. In an attempt to prepare a dinuclear anionic alkoxide which was hydrocarbon-soluble and which would give a simple  $^1\text{H}$  n.m.r. spectrum we allowed  $\text{Be}(\text{OSiMe}_3)_2$  (see below) to react with  $\text{LiOSiMe}_3$ , since the latter is over one thousand times more soluble in toluene than its *t*-butoxy-analogue.<sup>7</sup> The complex  $[\text{LiBe}(\text{OSiMe}_3)_3]_2$  is soluble and dimeric in benzene solution and its  $^1\text{H}$  n.m.r. spectrum in carbon tetrachloride consists of single equal-area resonances at  $\tau$  9.82, 9.84, and 9.89 indicative of a structure with three types of trimethylsilyloxy-groups. A structure with beryllium, lithium, and oxygen atoms located at corners of a cube (I) has three



non-equivalent alkoxide groups in equal number, two being terminal, two bridging two beryllium and one lithium atoms, and two bridging two lithium and one beryllium atoms. This geometry allows each beryllium and oxygen atom to maximise its co-ordination number, both beryllium and oxygen being four-co-ordinate and lithium being three-co-ordinate. Tetranuclear  $[\text{MeBeOSiMe}_3]_4$  has been shown by crystallography to have a similar geometry, MeBe groups replacing Li atoms in (I).<sup>8</sup>

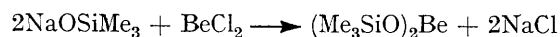
<sup>4</sup> N. A. Bell and G. E. Coates, *J. Chem. Soc. (A)*, 1968, 628.

<sup>5</sup> H. Meerwein and T. Bersin, *Annalen*, 1929, **476**, 113.

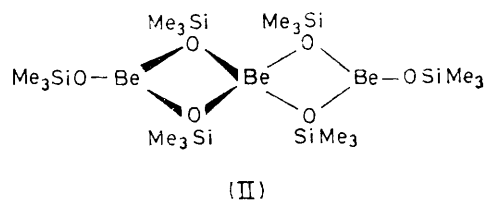
<sup>6</sup> E. Weiss and R. Wolfrum, *J. Organometallic Chem.*, 1968, **12**, 257.

<sup>7</sup> H. Schmidbaur and J. Adlkofer, *Chem. Ber.*, 1972, **105**, 1956.

Bis(trimethylsilyloxy)beryllium is readily soluble in benzene and trimeric in that solvent. Though the  $^1\text{H}$



n.m.r. spectrum in benzene is complex, more resonances being observed than can be accounted for on the basis of a simple single arrangement of atoms, the spectrum in carbon tetrachloride is greatly simplified; two resonances in a 2 : 1 area ratio at  $\tau$  9.78 and 9.92, respectively, suggest the linear structure (II) similar to that proposed for the trimeric carbon analogue.<sup>9</sup> It is noteworthy that the spectrum of  $[\text{Be}(\text{OBu}^t)_2]_3$  in  $\text{CCl}_4$  is identical to that



previously described for the trimer in  $\text{C}_7\text{D}_{14}$ . In contrast, the spectrum in benzene solution recorded at 100 MHz consists of two resonances at  $\tau$  8.44 and 8.45, which of course would not have been resolved in the earlier measurements at 60 MHz. Finally, the  $^9\text{Be}$  n.m.r. spectrum of the *t*-butoxide, recorded at 14.05 MHz, consists of two resonances at  $-1.8$  p.p.m. and  $+1.3$  p.p.m. relative to aqueous  $\text{Be}(\text{NO}_3)_2$ .

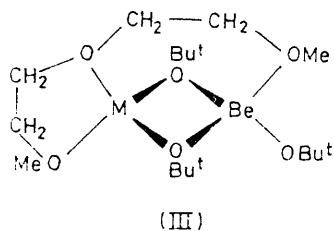
In contrast to the perceptible solubility of  $\text{LiBe}(\text{OBu}^t)_3$  in benzene, the sodium, potassium, and caesium analogues are insoluble in that solvent. Crystalline (by X-ray powder diffraction) sodium tri-*t*-butoxyberyllate crystallises from an equimolar mixture of  $\text{NaOBu}^t$  and  $\text{Be}(\text{OBu}^t)_2$  in tetrahydrofuran, though it was also prepared rather less straightforwardly from  $\text{Na}_2\text{BeH}_4$  and an excess of *t*-butyl alcohol without a molecule of alcohol of solvation being incorporated (contrast the methoxy-analogue). The potassium analogue,  $\text{KBe}(\text{OBu}^t)_3$ , is readily prepared from  $\text{KOBu}^t$  and  $\text{Be}(\text{OBu}^t)_2$ , or from potassium metal and beryllium di-*t*-butoxide in *t*-butyl alcohol. The potassium complex crystallises from tetrahydrofuran. The caesium complex is insoluble in diethyl ether. The rubidium complex, however, readily crystallises from benzene, though it is not sufficiently soluble in that solvent to determine its molecular weight cryoscopically. We suggest the alkali-metal tri-*t*-butoxyberyllate complexes are isostructural, their i.r. spectra being very similar. Based on (I), their general insolubility then would be due to intermolecular interactions between electropositive atoms of one cube with electronegative atoms of those of another. Indeed, crystal structure analysis of hydrocarbon-insoluble, tetrahydrofuran soluble,  $\text{KOBu}^t$  shows three co-ordinate potassium and four co-ordinate oxygen atoms located at corners of

<sup>8</sup> D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem.*, 1969, **81**, 398.

<sup>9</sup> G. E. Coates and A. H. Fishwick, *J. Chem. Soc. (A)*, 1968, 477.

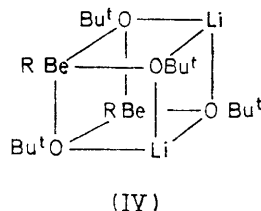
a cube, the rubidium and caesium congeners being isostructural.<sup>10</sup>

In no case have we been able to isolate 2 : 1 complexes  $M_2Be(OBu^t)_4$ ; apparently four t-butoxy-groups are too large to fit comfortably about one beryllium atom. We have prepared two co-ordination complexes with bis(2-methoxyethyl) ether, lithium tri-t-butoxyberyllate-bis-(2-methoxyethyl) ether and its sodium analogue. Since both complexes are easily soluble in hydrocarbon solvents and are monomeric in benzene solution, the structure (III;  $M = Li, Na$ ) is suggested, both metal atoms being four co-ordinate, rather than a salt-like constitution,



$[M(C_6H_{14}O_3)_2][Be(OBu^t)_3]^-$ . The complex (III) might be viewed as  $MOBu^t(C_6H_{14}O_3)$  acting as a base to  $Be(OBu^t)_2$ , suggesting its base strength is comparable to that of 4-dimethylaminopyridine and greater than that of 1-azabicyclo[2.2.2]octane (quinuclidine), since the former gives monomeric  $(Bu^tO)_2Be, 4-Me_2NC_5H_4N$ ,<sup>11</sup> though  $[Be(OBu^t)_2]_3$  is recovered from the latter.<sup>12</sup>

t-Butyl-lithium reacts with  $Be(OBu^t)_2$  yielding dimeric  $[LiBu^tBe(OBu^t)_2]_2$ . The  $^1H$  n.m.r. spectrum (benzene solution, the complex reacts with  $CCl_4$  giving a white solid) consists of two resonances at  $\tau$  8.66 and 8.70 in a 2 : 1 ratio, consistent with (IV;  $R = Bu^t$ ). The ethyl homologue, from  $EtLi$  and  $Be(OBu^t)_2$ , is also dimeric and



likely has a similar structure (IV;  $R = Et$ ). Lithium t-butyl-di-t-butoxyberyllate reacts with bis(2-methoxyethyl) ether giving monomeric  $LiBu^tBe(OBu^t)_2(C_6H_{14}O_3)$  (III;  $M = Li$ ) the terminal t-butoxy-group being replaced by a t-butyl group. An equimolar mixture of  $Bu^tLi$  and  $Be(OC_2Et_3)_2$  yields  $LiBu^tBe(OC_2Et_3)_2$  whose degree of association is between 1 and 2. From the degree of association measured cryoscopically in benzene, viz., 1.87, 1.41, and 1.04 weight % concentration, the equilibrium constant for the reaction  $[LiBu^tBe(OC_2Et_3)_2]_2 \rightleftharpoons 2[LiBu^tBe(OC_2Et_3)_2]$  was calculated as 0.0030, 0.0028, and 0.0035 mol l<sup>-1</sup>. A monomer-trimer equilibrium would have resulted in a much bigger change

<sup>10</sup> E. Weiss, H. Alsdorf, H. Kühr, and H. F. Grützmaier, *Chem. Ber.*, 1968, **101**, 3777.

<sup>11</sup> R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1972, 2153.

<sup>12</sup> R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1974, 1171.

of apparent equilibrium constant with concentration. The existence of the equilibrium is likely due to steric interference between t-butyl and  $Et_3CO$  groups in the dimer.

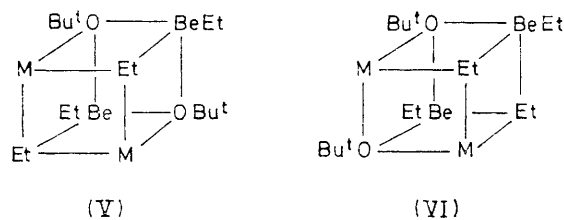
Whereas  $LiBe(OBu^t)_3$  does not react with  $LiOBu^t$  it was of interest to find that it reacts with  $Bu^tLi$ , giving trinuclear  $Li_2Bu^tBe(OBu^t)_2$  whose degree of association is between 1 and 2 in benzene solution. The concentration dependence of its molecular weight suggests a 2 monomer  $\rightleftharpoons$  dimer equilibrium similar to that described for  $LiBu^tBe(OC_2Et_3)_2$ .

The remarkable change in solubility properties with alkali-metal atom is illustrated by the benzene-insolubility of  $NaEtBe(OBu^t)_2$ , the lithium analogue being easily soluble.

Sodium t-butoxide dissolves in an ether solution of diethylberyllium yielding  $[NaEt_2Be(OBu^t)]_2$ . In contrast, an equimolar mixture of  $LiOBu^t$  and  $Et_2Be$  gives a liquid, which on distillation yields liquid  $EtBeOBu^t$  as the only volatile product. The degree of association of the liquid alkoxide is between 2 and 3. The equilibrium constants extracted from the molecular weight data of 0.16 and 0.12 mol l<sup>-1</sup> for 1.48 and 1.06 weight % concentration, respectively, support a tetramer  $\rightleftharpoons$  2(dimer) equilibrium.

Isolation of ethylberyllium t-butoxide from reaction of  $Bu^tOLi$  with  $Et_2Be$  suggests to us that the structural

unit in these dimers consists of two  $M \begin{matrix} \diagup O \\ \diagdown Et \end{matrix} BeEt$  units connected by alkoxy- and alkyl-groups. Two possible isomers are (V) or (VI),  $M = Li$  or  $Na$ . We



prefer the latter as one of the electropositive alkali-metal atoms has two electronegative oxygen atoms and one ethyl group as nearest neighbours whereas (V) has each alkali-metal atom surrounded by one oxygen and two carbon atoms. The bridging ethyl group is then a four-centre two-electron bond, an electronic structure analogous to that of  $[MeLi]_4$ .<sup>13</sup> Further, (VI) allows each beryllium and oxygen atom to be four-coordinate saturated and each Group I atom to be three-coordinate. The solubility in hydrocarbons is now readily accounted for, the large t-butyl and ethyl groups preventing intermolecular contacts between neighbouring aggregates. An alternative structure similar to that found for the dimeric unit in the diethyl ether complex of sodium diethylberyllium hydride,<sup>14</sup> an hydrogen atom and ether

<sup>13</sup> E. Weiss and E. A. C. Lucken, *J. Organometallic Chem.*, 1964, **2**, 197.

<sup>14</sup> G. W. Adamson and H. M. M. Shearer, *Chem. Comm.*, 1965, 240.

group being replaced by a *t*-butoxy-group, is thought to be unlikely since the sodium atom would be only two- and the oxygen atom five-co-ordinate.

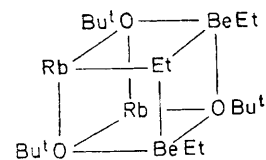
The  $^1\text{H}$  n.m.r. spectrum of the sodium complex (VI;  $\text{M} = \text{Na}$ ) in  $\text{C}_7\text{D}_8$  contains a quartet centred at  $\tau$  8.47 and a triplet centred at  $\tau$  10.35 due to the methyl and methylene groups, respectively. Lowering the temperature to  $-80^\circ$  causes the resonances to collapse into broad (12 Hz half-width at half-height) single lines at  $\tau$  8.35 and at 10.49, respectively. The process which exchanges the bridging- for terminal-ethyl groups is rapid, even at this low temperature.

We reasoned that the potassium analogue,  $(\text{KEt}_2\text{BeOBu}^t)_2$ , which crystallised ether-free from  $\text{KOBu}^t$  and  $\text{Et}_2\text{Be}$  in ether, might be considerably less stereochemically rigid, the across-ring potassium-beryllium distance being uncomfortably close causing the four-membered BeCKO rings to pucker, thereby lengthening and weakening metal-ligand bonds. Much to our surprise the complex dissolves in  $\text{C}_7\text{D}_8$  with formation of an orange solution, though the  $^1\text{H}$  n.m.r. spectrum is identical to that observed for a colourless benzene solution. Boiling the orange solution for a few minutes gives a red solution from which red crystals grow on the side of the  $^1\text{H}$  n.m.r. tube. Further, removal of solvent from the orange solution under reduced pressure yields the white dimer, the orange colour presumably being due to a solvent-solute interaction. Adapting this reaction to a larger scale (using toluene), we obtained red crystals of a substance in low yield. Measurement of the gas evolved in a vacuum system gave ethane as the only volatile material albeit in low yield, showing that proton abstraction from the solvent occurred. Carbonation of the red solid yielded phenylacetic acid, alkyl group metallation as opposed to nuclear metallation having taken place. The red solid is then best regarded as a benzyl derivative,  $\text{K}_5\text{Et}_3\text{Be}_3(\text{OBu}^t)_4(\text{benzyl})_4$ , the colour presumably then being due to the benzyl anion or near-anion (at least we expect that the benzyl groups carry an appreciable negative charge). So the anionic alkoxide  $[\text{KEt}_2\text{BeOBu}^t]_2$ , is a hydrocarbon-soluble metallating agent or 'protophile'.<sup>15</sup> The literature holds many examples of increased reactivity of an organometallic compound of the alkali metals when co-ordinated to nitrogen- or oxygen-donor atoms relative to the base-free compound. Of particular interest is metallation of toluene at normal temperature by an equimolar mixture of *n*-butyl-lithium and potassium *t*-butoxide, phenylacetic acid being isolated after reaction with carbon dioxide in 71% yield.<sup>16</sup>

Reaction of the potassium complex (VI;  $\text{M} = \text{K}$ ) with refluxing mesitylene yields an orange-red mesitylene-insoluble compound,  $\text{K}_3\text{Et}_2\text{Be}_2(\text{OBu}^t)_2(\text{mesityl})_2$ . In this instance the metallation occurs at the nucleus, since carbonation yields 2,4,6-trimethylbenzoic acid. This is peculiar because ethylsodium metallates the alkyl side

chain of mesitylene giving 3,5-dimethylphenylacetic acid and toluene giving phenylacetic acid, after carbonation with carbon dioxide.<sup>17</sup> The oxidation state of the mesityl groups in this complex appears to be  $-1.5$ ; though this is peculiar, the analytical data support the formula given. The solid compound, moreover, is diamagnetic, which is surprising in view of the apparent oxidation state of the mesityl groups. Again it is surprising that mesitylene is metallated at the nucleus in contrast to the metallation of the methyl group of toluene; we can explain neither this nor do we wish to speculate on the structures of these curious compounds, except to refer to the possibility that some of the mesityl groups might perhaps be both  $\sigma$ - and  $\pi$ -bound to one or more metal atoms, mesitylene forming stronger  $\pi$ -complexes than toluene.

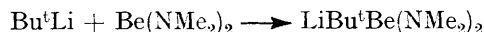
Equimolar mixtures of  $\text{RbOBu}^t$  and  $\text{Et}_2\text{Be}$  in diethyl ether yield a new type of complex  $\text{Rb}_2\text{Et}_3\text{Be}_2(\text{OBu}^t)_3$ . The  $^1\text{H}$  n.m.r. spectrum contains two distinct methylene quartets centred at  $\tau$  9.86 and 10.17, respectively, the area ratio being approximately 2:1, consistent with (VII). The rubidium may be mainly ionically bound.



(VII)

This tetranuclear complex reacts with boiling mesitylene yielding a red substance  $\text{Rb}_3\text{Et}_3\text{Be}_3(\text{OBu}^t)_2(\text{mesityl})_4$ , which reacts with  $\text{CO}_2$  yielding after hydrolysis 3,5-dimethylphenylacetic acid, the oxidation state of the mesityl again being apparently  $-1.5$ .

In view of the existence of the series  $\text{MRBe}(\text{OR}')_2$  described above, it seems likely that a similar series with dialkylamido- instead of an alkoxide group should be capable of existence. One of these has now been prepared:



The sparing benzene-solubility suggests an oligomeric or salt-like constitution, the latter being found for  $\text{KBe}(\text{NH}_2)_3$ .<sup>18</sup> In this context, it is noteworthy that we prepared bis(dimethylamido)beryllium from  $\text{BeCl}_2$  and  $\text{LiNMe}_2$  in 45% yield, since previous preparations using this reaction gave 5–6% yields.<sup>19</sup>

Since sodium hydride dissolves in an ether solution of diethylberyllium giving the ether complex of sodium diethylberyllium hydride,<sup>1</sup> we stirred sodium hydride with  $[\text{Be}(\text{OBu}^t)_2]_3$  in 1,2-dimethoxyethane. Hydrolysis of an aliquot of solution yielded no hydrogen. Though a solution in tetrahydrofuran yielded, on hydrolysis, hydrogen and beryllium in 1:2 ratio, extraction with tetrahydrofuran yielded a brown solution doubtless due to decomposition. Even KH failed to dissolve in

<sup>15</sup> D. Bryce-Smith, *J. Chem. Soc.*, 1954, 1079.

<sup>16</sup> M. Schlosser, *J. Organometallic Chem.*, 1967, 8, 9.

<sup>17</sup> P. Schorigin, *Chem. Ber.*, 1910, 43, 1938.

<sup>18</sup> L. Brisseau, M. G. B. Drew, and J. E. Goulter, *J.C.S. Chem. Comm.*, 1972, 918.

<sup>19</sup> A. H. Fishwick, Thesis, University of Durham, July 1967.

$\text{Be}(\text{OBU}^t)_2$  in tetrahydrofuran. The stability of the  $\text{Be}_3\text{O}_4$  structural unit, previously shown by the existence of the series  $\text{X}_2\text{Be}_3(\text{OBU}^t)_4$ ,<sup>20</sup> is evident. Even methylberyllium *t*-butoxide, which is dimeric in dilute refluxing diethyl ether (the metal thus being only three-co-ordinate), failed to react with sodium hydride. To our surprise, the m.p. of the product, whose i.r. and  $^1\text{H}$  n.m.r. spectra were identical to those of  $[\text{MeBeOBU}^t]_4$ , was 185–195° (decomp.), in contrast to the previously reported 93°. The melting behaviour of a sample prepared, as previously described, from  $\text{Me}_2\text{Be}$  and  $\text{Be}(\text{OBU}^t)_2$  in toluene, is rather more complex than previously noted, *i.e.*, it turns to a jelly-like substance at *ca.* 90° (possibly due to a phase change) and melts to a clear liquid in the range 170–195°.

#### EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenk tube, vacuum-line, and glove-box techniques. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method<sup>21</sup> under standard conditions. Potassium and rubidium were quantitatively precipitated as their tetraphenylborate salts.<sup>22</sup> Alkoxy-groups were in some instances determined by isolation and weighing of the alcohol formed during hydrolysis. Other components were determined by well established methods.  $^1\text{H}$  N.m.r. spectra were recorded at 100 MHz, with benzene as solvent and internal reference ( $\tau$  2.73) unless otherwise stated.  $^9\text{Be}$  N.m.r. spectra were recorded at 14.05 MHz with benzene as solvent and external aqueous  $\text{Be}(\text{NO}_3)_2$  as reference (0 p.p.m.). Some of the compounds described below decompose when heated without melting. In many such cases the main i.r. absorptions are quoted for characterisation; these were recorded as Nujol mulls, except where noted. Many of the compounds described below are sensitive to water and some to air, and to minimise the number of transfers from one apparatus to another, *e.g.* for weighing, yields were in general not recorded. Except when noted, yields were, apart from transfer losses, nearly quantitative.

#### Alkali-metal Trialkoxyberyllates

*Lithium Tri-t-butoxyberyllate.*—Lithium *t*-butoxide<sup>23</sup> (0.72 g, 0.0090 mol) in diethyl ether (15 ml) was added to beryllium di-*t*-butoxide<sup>9,24</sup> (1.4 g, 0.0090 mol) in diethyl ether (15 ml). After 15 min the diethyl ether was evaporated and the residue was crystallised from benzene as colourless plates, m.p. 212–213° (decomp.) (Found: hydrolysable  $\text{Bu}^t\text{O}$ , 93.0; Be, 4.0%.  $\text{C}_{12}\text{H}_{27}\text{BeLiO}_3$  requires hydrolysable  $\text{Bu}^t\text{O}$ , 93.3; Be, 3.8%).

*Sodium Tri-t-butoxyberyllate.*—*A, From sodium t-butoxide and beryllium di-t-butoxide.* Sodium *t*-butoxide<sup>25</sup> (0.88 g, 0.0088 mol) in diethyl ether (20 ml) was added to beryllium di-*t*-butoxide (1.4 g, 0.0090 mol) in diethyl ether (10 ml). After addition, the suspension was stirred for 15 min, ether was evaporated, and the residue was crystallised from tetrahydrofuran, m.p. 213–214° (decomp.) (Found: hydrolysable  $\text{Bu}^t\text{O}$ , 84.0; Be, 3.3%.  $\text{C}_{12}\text{H}_{27}\text{BeNaO}_3$  requires hydrolysable  $\text{Bu}^t\text{O}$ , 84.0; Be, 3.6%).

<sup>20</sup> R. A. Andersen, N. A. Bell, and G. E. Coates, *J.C.S. Dalton*, 1972, 577.

<sup>21</sup> D. A. Everest, 'The Chemistry of Beryllium,' Elsevier, Amsterdam, 1964, p. 120.

<sup>22</sup> K. Sporek and A. F. Williams, *Analyst*, 1955, 80, 347.

contained absorptions at 1351m, 1221s, 1202s, 1040s, 1015m, 981m, 885m, 847w, 735w, 715w, 580w, 530w, 465w, and 455w  $\text{cm}^{-1}$ .

*B, From sodium diethyl-t-butoxyberyllate and t-butyl alcohol.* *t*-Butyl alcohol (0.39 g, 0.0053 mol) in diethyl ether (10 ml) was added to  $\text{NaEt}_2\text{BeOBU}^t$  (0.86 g, 0.0053 mol) in diethyl ether (20 ml) at  $-78^\circ$ . After addition, the solution was warmed to room temperature. At *ca.* 0° a white solid began to form. The suspension was stirred for 15 min, ether was evaporated, and the residue crystallised from tetrahydrofuran, m.p. 215–217° (decomp.). The i.r. spectrum was identical to that of the product obtained by method A, above.

*C, From di-sodium beryllium hydride and t-butyl alcohol (preparation by Dr. N. A. Bell).* Tetrahydrofuran, *t*-butyl alcohol (*ca.* 1.0 g), and  $\text{Na}_2\text{BeH}_4$  (0.097 g, 0.0016 mol) were stirred until gas evolution ceased. The solution was filtered and the volatile material was removed in vacuum. The resulting white residue had an i.r. spectrum identical to that of the product obtained by method A, above.

*Potassium Tri-t-butoxyberyllate.*—*A, From potassium, t-butyl alcohol, and beryllium di-t-butoxide.* Potassium (0.28 g, 0.0071 g-atom), beryllium di-*t*-butoxide (0.55 g, 0.0035 mol), and *t*-butyl alcohol (20 ml) were stirred for 12 h. Initially, the solution was colourless but after 12 h a dense white suspension had formed. The volatile material was removed in vacuum, tetrahydrofuran (15 ml) was added, and the suspension was filtered. Tetrahydrofuran was removed from the filtrate and the residue was recrystallised from tetrahydrofuran as white needles, m.p. 162–163° (Found: hydrolysable  $\text{Bu}^t\text{O}$ , 81.6; Be, 3.2%.  $\text{C}_{12}\text{H}_{27}\text{BeKO}_3$  requires hydrolysable  $\text{Bu}^t\text{O}$ , 81.1; Be, 3.4%). The i.r. spectrum consisted of absorptions at 1354s, 1350m, 1216s, 1203s, 1055s, 1010m, 1000m, 878m, 847m, 730w, 712w, 576w, 530s, 468w, and 450w  $\text{cm}^{-1}$ .

*B, From potassium t-butoxide and beryllium di-t-butoxide.* Beryllium di-*t*-butoxide (0.7 g, 0.0045 mol) in diethyl ether (10 ml) was added to potassium *t*-butoxide<sup>5</sup> (0.50 g, 0.0045 mol) in tetrahydrofuran (20 ml). After addition, the solution was stirred for 15 min, volatile material was evaporated, and the residue was crystallised from tetrahydrofuran, m.p. 162–163°. The i.r. spectrum was identical to that of the product obtained by method A, above.

*Rubidium Tri-t-butoxyberyllate.*—Beryllium di-*t*-butoxide (1.1 g, 0.0071 mol) in tetrahydrofuran (10 ml) was added to a suspension of rubidium *t*-butoxide (1.1 g, 0.0071 mol) in tetrahydrofuran (20 ml). After 12 h the suspension was filtered, solvent was removed from the filtrate, and the yellow solid was crystallised as pale yellow prisms, from benzene, m.p. 145–147° (decomp.) (Found: hydrolysable  $\text{Bu}^t\text{O}$ , 70.0; Be, 3.1%.  $\text{C}_{12}\text{H}_{27}\text{BeO}_3\text{Rb}$  requires hydrolysable  $\text{Bu}^t\text{O}$ , 69.8; Be, 2.9%).

*Caesium Tri-t-butoxyberyllate.*—Di-*t*-butoxyberyllium (0.44 g, 0.0029 mol) in diethyl ether (10 ml) was added to caesium *t*-butoxide (0.59 g, 0.0029 mol) suspended in diethyl ether (10 ml). After addition, the suspension was stirred for 1 h, the product was collected, washed with diethyl ether ( $3 \times 10$  ml), and dried in vacuum for 2 h, softened at *ca.* 175° and melted at 179–181°. The yield was 0.64 g, 78% (Found: hydrolysable  $\text{Bu}^t\text{O}$ , 60.5; Be, 2.4%.  $\text{C}_{12}\text{H}_{27}\text{BeCsO}_3$  requires hydrolysable  $\text{Bu}^t\text{O}$ , 60.7; Be, 2.5%).

<sup>23</sup> C. W. Kamiński and D. H. Lewis, *J. Org. Chem.*, 1965, 30, 3498.

<sup>24</sup> N. A. Bell and G. E. Coates, *J. Chem. Soc. (A)*, 1968, 823.

<sup>25</sup> H. Feuer, J. W. Shephard, and C. Savides, *J. Amer. Chem. Soc.*, 1956, 78, 4364.

*Lithium Tri(trimethylsiloxy)beryllate*.—Bis(trimethylsiloxy)beryllium (see below) (1.2 g, 0.0063 mol) in hexane (10 ml) was added to lithium trimethylsiloxy<sup>26</sup> (0.60 g, 0.0063 mol) in hexane (5 ml). After addition, a white precipitate slowly formed which was stirred 12 h. Hexane was evaporated and the residue crystallised from toluene as waxy plates in 67% yield (1.2 g), shrank at *ca.* 160°, melted at 172–179°. The complex sublimed in vacuum at 110–115° [Found: hydrolysable Me<sub>3</sub>SiO, 93.5; Be, 3.3%; *M* (cryoscopically, 1.95 and 1.40% w/w in benzene), 585 and 566. C<sub>18</sub>H<sub>54</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>6</sub>Si<sub>6</sub> requires hydrolysable Me<sub>3</sub>SiO, 94.4; Be, 3.2%; *M*, 566]. The <sup>1</sup>H n.m.r. spectrum (CCl<sub>4</sub> with 5% v/v C<sub>6</sub>H<sub>6</sub> as internal reference) consisted of singlets at τ 9.82, 9.84, and 9.89 in area ratio 1 : 1 : 1.

*Bis(trimethylsiloxy)beryllium*, [Be(OSiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>.—Sodium trimethylsiloxy<sup>27</sup> (41.9 g, 0.374 mol) in diethyl ether (100 ml) was added to the bis(diethyl ether) complex of beryllium chloride (42.6 g, 0.187 mol) in diethyl ether (150 ml). After addition, the suspension was stirred for 1 h, filtered, and diethyl ether was removed in vacuum from the filtrate. The pale yellow residue was sublimed 80–85°, 10<sup>-2</sup> mmHg. The yield (21.0 g) was 60%. When heated it shrank *ca.* 55°, softened *ca.* 65°, and melted 69–72° [Found: hydrolysable Me<sub>3</sub>SiO, 95.2; Be, 4.6%; *M* (cryoscopically, 2.76 and 1.93% w/w in benzene), 559 and 557. C<sub>18</sub>H<sub>54</sub>Be<sub>3</sub>O<sub>6</sub>Si<sub>6</sub> requires hydrolysable Me<sub>3</sub>SiO, 95.2; Be, 4.8%; *M*, 561]. The <sup>1</sup>H n.m.r. spectrum (CCl<sub>4</sub> with 5% v/v C<sub>6</sub>H<sub>6</sub> as internal reference) consisted of single resonances at τ 9.78 and 9.92 in area ratio 2 : 1.

*Lithium Di-t-butoxy-2-methylbutoxyberyllate*, [LiBe(OBu<sup>t</sup>)<sub>2</sub>(OCMe<sub>2</sub>Et)]<sub>2</sub>.—Beryllium di-t-butoxy (1.4 g, 0.0089 mol) in diethyl ether (15 ml) was added to lithium 2-methylbutoxy (0.84 g, 0.0089 mol) in diethyl ether (15 ml). After stirring for 1 h, diethyl ether was evaporated, and the residue was sublimed 75–80°, 10<sup>-2</sup> mmHg, m.p. 138–140° [Found: Be, 3.7%; hydrolysable Bu<sup>t</sup>O and Me<sub>2</sub>EtCO, 0.108 g from 0.116 g of complex; *M* (cryoscopically 4.44 and 3.36% w/w in benzene), 564 and 563. C<sub>26</sub>H<sub>58</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>6</sub> requires Be, 3.6%; hydrolysable Bu<sup>t</sup>O and Me<sub>2</sub>EtCO, 0.109 g; *M*, 498].

*Lithium Tri(2-methylbutoxy)beryllate*, [LiBe(OCMe<sub>2</sub>Et)]<sub>3</sub>.—Bis(2-methylbutoxy)beryllium<sup>11</sup> (2.1 g, 0.012 mol) in diethyl ether (15 ml) was added to lithium 2-methylbutoxy (1.1 g, 0.012 mol) in diethyl ether (15 ml). After stirring for 15 min, solvent was evaporated, and the viscous liquid was sublimed as a waxy deposit onto a water-cooled cold-finger at 100–110°, 10<sup>-2</sup> mmHg, m.p. 56–57° [Found: hydrolysable Me<sub>2</sub>EtCO, 94.7; Be, 3.3%; *M* (cryoscopically 2.34 and 2.08% w/w in benzene), 555 and 560. C<sub>30</sub>H<sub>66</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>6</sub> requires hydrolysable Me<sub>2</sub>EtCO, 94.6; Be, 3.3%; *M*, 552].

*Lithium Tri-t-butoxyberyllate-Bis(2-methoxyethyl) Ether Complex*.—Lithium tri-t-butoxyberyllate (1.0 g, 0.0042 mol) was dissolved in bis(2-methoxyethyl) ether (3 ml). After stirring for 15 min, solvent was removed in vacuum, and the residue crystallised from hexane as rectangular prisms, m.p. 69–70° [Found: hydrolysable Bu<sup>t</sup>O, 59.0; Be, 2.5%; *M* (cryoscopically 1.43 and 1.07% w/w in benzene), 343 and 341. C<sub>18</sub>H<sub>41</sub>BeLiO<sub>6</sub> requires hydrolysable Bu<sup>t</sup>O, 59.4; Be, 2.4%; *M*, 369]. The <sup>1</sup>H n.m.r. spectrum consists of a multiplet centred at τ 6.80 due to ether protons and a singlet at τ 8.35 due to Bu<sup>t</sup>O-protons in area ratio 1.0 : 1.9.

*Sodium Tri-t-butoxyberyllate-Bis(2-methoxyethyl) Ether*

<sup>26</sup> H. Schmidbaur, J. A. Perez-Garcia, and H. S. Arnold, *Z. anorg. Chem.*, 1964, **328**, 105.

*Complex*.—Sodium tri-t-butoxyberyllate (1.0 g, 0.0040 mol) was dissolved in bis(2-methoxyethyl) ether (5 ml). After stirring 15 min, solvent was removed in vacuum, and the residue crystallised from benzene as colourless needles, m.p. 82–83° [Found: hydrolysable Bu<sup>t</sup>O, 56.0; Be, 2.3%; *M* (cryoscopically 0.63 and 0.48% w/w in benzene), 365 and 354. C<sub>18</sub>H<sub>41</sub>BeNaO<sub>6</sub> requires hydrolysable Bu<sup>t</sup>O, 56.9; Be, 2.3%; *M*, 385]. The <sup>1</sup>H n.m.r. spectrum consists of single resonances at τ 6.78 (MeOCH<sub>2</sub><sup>-</sup>), one at τ 7.02 (MeOCH<sub>2</sub><sup>-</sup>), and one at τ 8.30 (Bu<sup>t</sup>O) in area ratio 1.0 : 1.4 : 4.6.

#### Alkali-metal Alkyldialkoxyberyllates

*Lithium Ethyl-di-t-butoxyberyllate*.—Ethyl-lithium (5.6 ml of a 1.3M solution in benzene, 0.0069 mol) was added to beryllium di-t-butoxy (1.1 g, 0.0069 mol) in hexane (10 ml). After stirring the turbid solution for 1 h, the solvents were removed in vacuum and the residue was crystallised as white needles from hexane-benzene (4 : 1) in quantitative yield, m.p. 97–98° [Found: hydrolysable ethyl, 15.7; hydrolysable Bu<sup>t</sup>O, 77.4; Be, 4.5%; *M* (cryoscopically 1.36 and 0.97% w/w in benzene), 389 and 391. C<sub>20</sub>H<sub>46</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>4</sub> requires hydrolysable ethyl, 15.2; hydrolysable Bu<sup>t</sup>O, 76.5; Be, 4.7%; *M*, 382].

*Sodium Ethyl-di-t-butoxyberyllate*.—Ethylberyllium t-butoxy (0.56 g, 0.0050 mol) in diethyl ether (5 ml) was added to sodium t-butoxy (0.48 g, 0.0050 mol) in diethyl ether (10 ml). After stirring for 30 min, the suspension was filtered, diethyl ether was removed from the filtrate, and the residue crystallised from toluene as colourless prisms in 15% yield (0.15 g), shrank at *ca.* 100°, melted 172–174° (decomp.) (Found: hydrolysable ethyl, 13.6; Be, 4.4%. C<sub>10</sub>H<sub>23</sub>BeNaO<sub>2</sub> requires hydrolysable ethyl, 14.0; Be, 4.4%).

*Lithium t-Butyl-di-t-butoxyberyllate*.—t-Butyl-lithium (6.3 ml of a 1.2M pentane solution, 0.0078 mol) was added to di-t-butoxyberyllium (1.2 g, 0.0078 mol) in hexane (5 ml). After addition, the white precipitate was stirred for 1 h, solvents were removed in vacuum, and the residue was crystallised from benzene as large white plates. When heated, it turned to a turbid white liquid at 174–175° [Found: hydrolysable butyl, 26.0; Be, 4.3%; *M* (cryoscopically 1.04 and 0.78% w/w in benzene), 433 and 441. C<sub>24</sub>H<sub>54</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>4</sub> requires hydrolysable butyl, 26.0; Be, 4.1; *M*, 438]. The <sup>1</sup>H n.m.r. spectrum consisted of single resonances at τ 8.66 (Bu<sup>t</sup>O) and at τ 8.70 (Bu<sup>t</sup>-Be) in area ratio 2 : 1.

*Lithium t-Butyl-di-(3-ethylpentoxy)beryllate*, [LiBu<sup>t</sup>Be(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>.—t-Butyl-lithium (2.8 ml of a 1.2M pentane solution, 0.0034 mol) was added to bis(3-ethylpentoxy)beryllium<sup>11</sup> (0.81 g, 0.0034 mol) in hexane (3 ml). After stirring for 2 h, a white precipitate slowly formed, which was stirred for an additional 2 h. The volatile material was removed in vacuum and the residue was crystallised as colourless needles from benzene, shrank *ca.* 90°, melted 99° [Found: hydrolysable butyl, 18.5; Be, 3.1%; *M* (cryoscopically 1.87, 1.41, and 1.04% w/w in benzene), 482, 466, and 451. C<sub>36</sub>H<sub>78</sub>Be<sub>2</sub>Li<sub>2</sub>O<sub>4</sub> requires hydrolysable butyl, 18.8; Be, 3.0%; *M*, 606].

*Dilithium t-Butyltri-t-butoxyberyllate*.—t-Butyl-lithium (2.6 ml of a 1.2M pentane solution, 0.0032 mol) was added to a suspension of LiBe(OBu<sup>t</sup>)<sub>3</sub> (0.75 g, 0.0032 mol) in benzene (10 ml). The suspension slowly dissolved on stirring over 8 h. The volatile material was evaporated and the

<sup>27</sup> J. F. Hyde, O. K. Johansson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. R. Roche, *J. Amer. Chem. Soc.*, 1953, **75**, 5615.

residue was crystallised from benzene as colourless *prisms*, m.p. 170—172° [Found: hydrolysable butyl, 19.1; Be, 3.0%; *M* (cryoscopically 1.55, 1.17, 0.89% w/w in benzene), 460, 488, and 554.  $C_{32}H_{72}Be_2Li_4O_6$  requires hydrolysable butyl, 19.1; Be, 3.0%; *M*, 598]. The  $^1H$  n.m.r. spectrum consisted of a singlet at  $\tau$  8.57, one at  $\tau$  8.58, and one at  $\tau$  8.60 in area ratio 1.5 : 1.5 : 1.

*Lithium t-Butyl-di-t-butoxyberyllate-Bis(2-methoxyethyl Ether)*.—Lithium *t*-butyl-di-*t*-butoxyberyllate (0.50 g, 0.0023 mol) was dissolved in an excess of bis(2-methoxyethyl) ether. After stirring for 15 min, volatile matter was removed in vacuum, and the residue crystallised as waxy *plates* from hexane, m.p. 60° [Found: hydrolysable butyl, 15.5; Be, 2.7%; *M* (cryoscopically 1.67 and 1.26% w/w in benzene), 364 and 352.  $C_{18}H_{41}BeLiO_5$  requires hydrolysable butyl, 16.2; Be, 2.6%; *M*, 353]. The  $^1H$  n.m.r. spectrum consisted of a singlet at  $\tau$  6.77 due to  $MeOCH_2^-$ , one at  $\tau$  6.93 due to  $MeOCH_2^-$ , one at  $\tau$  8.36 due to  $Bu^t-Be^-$ , and one at  $\tau$  8.49 due to  $Bu^tO^-$  in area ratio 6 : 8 : 9 : 18.

#### Alkali-metal Dialkylalkoxyberyllates

*Sodium Diethyl-t-butoxyberyllate*.—Sodium *t*-butoxide (1.1 g, 0.0010 mol) in diethyl ether (10 ml) was added to the diethylberyllium-diethyl ether complex (1.3 g, 0.0011 mol) in diethyl ether (10 ml) at  $-78^\circ$ . After addition the solution was allowed to warm to room temperature and was stirred for 15 min. Diethyl ether was removed in vacuum and the residue was crystallised from benzene-hexane (1 : 1) as colourless *prisms*, softened *ca.* 85°, melted 94—95° [Found: hydrolysable ethyl, 35.4; Be, 5.7%; *M* (cryoscopically 0.86 and 0.64% w/w in benzene), 317 and 328.  $C_{16}H_{38}Be_2Na_2O_2$  requires hydrolysable ethyl, 35.6; Be, 5.5%; *M*, 326]. The  $^1H$  n.m.r. spectrum consists of a triplet centred at  $\tau$  8.42 ( $J$  8 Hz) due to  $CH_3CH_2^-$ , a singlet at  $\tau$  8.75 due to  $Bu^tO^-$ , and a quartet centred at  $\tau$  10.35 ( $J$  8 Hz) due to  $CH_3CH_2^-$  in area ratio 6 : 9 : 4.

*Potassium Diethyl-t-butoxyberyllate*.—Diethylberyllium-diethyl ether complex (0.87 g, 0.0062 mol) in diethyl ether (10 ml) was added to potassium *t*-butoxide (0.75 g, 0.0062 mol) suspended in diethyl ether (20 ml). After stirring for 30 min, the suspension was allowed to settle, was filtered, diethyl ether was evaporated from the filtrate, and the residue was crystallised from hexane-diethyl ether (10 : 1) [or from benzene-hexane (1 : 1)] as colourless waxy *prisms* in 29% (0.32 g) yield, m.p. 100—102° (decomp.) [Found: hydrolysable ethyl, 32.0; Be, 4.9%; *M* (cryoscopically 1.26 and 1.02% w/w in benzene), 336 and 357.  $C_{16}H_{38}Be_2K_2O_2$  requires hydrolysable ethyl, 32.4; Be, 5.0%; *M*, 358]. The  $^1H$  n.m.r. spectrum consists of a triplet centred at 8.49 ( $J$  8 Hz) due to  $CH_3CH_2^-$ , a singlet at  $\tau$  8.70 due to  $Bu^tO^-$ , and a quartet centred at  $\tau$  10.28 ( $J$  8 Hz) due to  $CH_3CH_2^-$ , in area ratio 6 : 9 : 4. The complex was dissolved in toluene (5 ml) and the orange solution was stirred for 3 h. Toluene was removed in vacuum and the white solid was identified as  $[KEt_2BeOBu^t]_2$  by m.p. 100—102° (decomp.) and mixed m.p. 103—105° (decomp.).

*Reaction of Lithium t-Butoxide with Diethylberyllium, [EtBeOBu^t]\_{2-4}*.—Diethylberyllium-diethyl ether complex (3.5 g, 0.025 mol) in diethyl ether (5 ml) was added to lithium *t*-butoxide (2.0 g, 0.025 mol) in diethyl ether (25 ml). After addition, the solution was stirred for 1 h, diethyl ether was evaporated, and the liquid residue was distilled (36—39°, diffusion pump vacuum, bath temperature 100—140°). The yield of colourless viscous liquid was 1.0 g (36%) [Found: hydrolysable ethyl, 25.7; Be, 7.8%; *M* (cryo-

scopically 1.48 and 1.06% w/w in benzene), 273 and 264.  $C_{24}H_{56}Be_4O_4$  requires hydrolysable ethyl, 26.1; Be, 8.1%; *M*, 444]. The i.r. spectrum of the neat liquid consists of absorptions at 2975s, 2935s, 2895s, 2855s, 2800m,sh, 2715w, 1470m, 1457m, 1410m, 1388s, 1365s, 1252s, 1228m,sh, 1202s, 1190s, 1137w, 1037s, 1005s, 950w, 932s, 912w, 855w, 823m, 713m, 615m, 597m, and 635m  $cm^{-1}$ .

In a separate experiment, the diethylberyllium-diethyl ether complex (0.65 g, 0.0074 mol) and beryllium di-*t*-butoxide (1.1 g, 0.0074 mol) were stirred 15 min in diethyl ether (20 ml). Diethyl ether was evaporated and the residue crystallised from hexane as colourless *prisms*, m.p. 36° [Found: hydrolysable ethyl, 17.2; Be, 7.2%; ratio 2.0 : 2.7].

*Reaction of Rubidium t-Butoxide with Diethylberyllium, Rb\_2Et\_2Be\_2(OBu^t)\_3*.—The diethylberyllium-diethyl ether complex (1.5 g, 0.011 mol) in diethyl ether (10 ml) was added to rubidium *t*-butoxide (1.7 g, 0.011 mol) suspended in diethyl ether (30 ml). After the brown suspension had been stirred for 1 h, it was allowed to settle, filtered, and diethyl ether was evaporated from the filtrate. The brown oil solidified on addition of hexane, and it crystallised from hexane-diethyl ether (1 : 1) [or benzene-hexane (1 : 1)] as pale tan *prisms*, yield 0.35 g (15%). When heated, it shrank *ca.* 125°, softened *ca.* 135°, and melted with decomposition at 180—185° [Found: hydrolysable ethyl, 17.0; hydrolysable  $Bu^tO$ , 44.4; Be, 3.8%; *M* (cryoscopically 1.49 and 1.07% w/w in benzene), 487 and 492.  $C_{18}H_{42}Be_2O_2Rb_2$  requires hydrolysable ethyl, 17.0; hydrolysable  $Bu^tO$ , 44.3; Be, 3.6%; *M*, 495]. The  $^1H$  n.m.r. spectrum consists of a multiplet centred at  $\tau$  8.38 due to methyl protons in the ethyl groups, a singlet at  $\tau$  8.64 ( $Bu^tO$ ), a quartet centred at  $\tau$  9.86 ( $J$  8 Hz), and one at  $\tau$  10.17 ( $J$  8 Hz), due to methylene protons of ethyl groups, the latter two quartets being in an area ratio *ca.* 1 : 2.

*Reaction of Potassium Diethyl-t-butoxyberyllate with Toluene*.—Boiling an orange toluene (10 ml) solution of  $KEt_2BeOBu^t$  (1.1 g, 0.0062 mol) for 15 min yielded a red solution from which red *prisms* (0.15 g) formed on cooling the solution to room temperature. On heating, it turned black *ca.* 200° without melting [Found: hydrolysable ethyl, 9.0; Be, 2.7; K, 20.4%; the ratio is 3.1 : 3.0 : 5.2, respectively. A sample of the substance was hydrolysed with 2N- $H_2SO_4$  and benzene (1 ml) was added to extract organic products. Examination of the benzene solution by  $^1H$  n.m.r. spectroscopy revealed resonances due to toluene and *t*-butyl alcohol in 1 : 1 ratio. The simplest empirical formula consistent with these data is  $K_5Et_3Be_3(OBu^t)_4(CH_2Ph)_4$ .  $C_{50}H_{79}Be_3K_5O_4$  requires hydrolysable ethyl, 9.0; Be, 2.9; K, 20.2%]. The i.r. spectrum consisted of absorptions at 1590s, 1578s, 1498m, 1485m,sh, 1353m, 1323m, 1278w, 1223w, 1198s, 1166s, 1138w, 1026s, 1011s, 954s, 833s, 832w, 799w, 758w, 713m, 695m, 593w, 563m, 528m, and 485m  $cm^{-1}$ . To the complex (0.09 g) in diethyl ether (20 ml) was added powdered solid carbon dioxide, resulting in immediate disappearance of the red colour. After stirring for 1 h, it was hydrolysed with 2N- $H_2SO_4$ , extracted with diethyl ether (3 × 10 ml), and dried over  $Na_2SO_4$ . Diethyl ether was evaporated and the residue (0.03 g) was identified as phenylacetic acid by m.p. 75—78° (lit.,<sup>28</sup> 75°).

In a separate experiment, toluene (1.02 g, 0.0111 mol) was added to  $KEt_2BeOBu^t$  (0.180 g, 0.00101 mol) at  $-196^\circ$  in a flask attached to a vacuum-line. On warming to room temperature and stirring for 12 h, the orange solution yielded an orange-brown solution and 0.0000612 mol of ethane.

<sup>28</sup> J. Houben and L. Keeselkaul, *Chem. Ber.*, 1902, **35**, 2523.

Heating the orange-brown solution to 95–100° for 1 h gave a further 0.000601 mol of ethane. Thus, 0.00101 mol  $\text{KEt}_2\text{BeOBu}^t$  yielded 0.000121 mol  $\text{C}_2\text{H}_6$ .

*With mesitylene.* The hydrocarbon (25 ml) was added to  $\text{KEt}_2\text{BeOBu}^t$  (1.7 g, 0.0067 mol) and the orange solution was boiled for 15 min. The colour changed progressively from orange to red-brown and the mixture yielded orange-red crystals (1.1 g) on cooling to room temperature. On heating, it turned black *ca.* 145° without melting [Found: hydrolysable ethyl, 10.2; Be, 3.0; K, 19.3%, the ratio being 2.1:2.0:3.0, respectively. A sample of the substance was hydrolysed with 2N- $\text{H}_2\text{SO}_4$  and benzene (1 ml) was added to extract organic products. Examination of the solution by  $^1\text{H}$  n.m.r. spectroscopy revealed resonances due to mesitylene and *t*-butyl alcohol in 1:1 ratio. The simplest empirical formula is  $\text{K}_3\text{Et}_2\text{Be}_2(\text{OBu}^t)_2(\text{mesityl})_2$ .  $\text{C}_{30}\text{H}_{50}\text{Be}_2\text{K}_3\text{O}_2$  requires hydrolysable ethyl, 10.1; Be, 3.1; K, 20.3%]. The i.r. spectrum consists of absorptions at 1605s, 1580s, 1528w, 1493w, 1402w, 1316m, 1337m, 1302m, 1270w, 1227m, 1201s, 1176m, 1168m, 1044m,sh, 1039s, 1016s, 963m, 887s, 837w, 805m, 761w, 739w,sh, 724m, 601w, 561m, 530w, 505w, and 479w  $\text{cm}^{-1}$ . Addition of powdered solid carbon dioxide to the substance (0.30 g) suspended in diethyl ether caused the red suspension to turn white. After stirring for 1 h, it was hydrolysed with 2N- $\text{H}_2\text{SO}_4$ , extracted with diethyl ether (3 × 10 ml), and the extract dried over  $\text{Na}_2\text{SO}_4$ . Ether was evaporated, yielding 0.11 g of 2,4,6-trimethylbenzoic acid identified by m.p. 149–151° (lit.,<sup>29</sup> 152°).

In a separate experiment,  $\text{KEt}_2\text{BeOBu}^t$  (0.178 g, 0.000995 mol) and mesitylene (0.358 g, 0.00298 mol) were mixed in a flask, attached to a vacuum-line, at –196°. The mixture was warmed to room temperature then heated at 130–135° for 5 min. The only volatile gas formed was ethane, 0.000682 mol.

*Reaction of (VII) with Mesitylene.*—Mesitylene (15 ml) was added to  $\text{Rb}_2\text{Et}_3\text{Be}_2(\text{OBu}^t)_3$  (1.2 g, 0.0024 mol) and the orange solution boiled 15 min. Cooling to room temperature yielded 0.80 g of red crystals from red mother liquors. On heating, it turned brown *ca.* 170° without melting [Found: hydrolysable ethyl, 7.1; Be, 2.2; Rb, 35.5%, ratio 3.0:3.0:5.1, respectively. A sample of the substance was hydrolysed with 2N- $\text{H}_2\text{SO}_4$  and the mixture was extracted with benzene (1 ml). Examination of the benzene solution by  $^1\text{H}$  n.m.r. spectroscopy showed resonances due to mesitylene and *t*-butyl alcohol in 2:1 ratio. The simplest empirical formula consistent with these data is  $\text{Rb}_5\text{Et}_3\text{Be}_3(\text{OBu}^t)_2(\text{mesityl})_4$ .  $\text{C}_{50}\text{H}_{77}\text{Be}_3\text{O}_2\text{Rb}_5$  requires hydrolysable ethyl, 7.5; Be, 2.3; Rb, 36.7%]. The i.r. spectrum consists of absorptions at 1604w, 1578s, 1525w, 1355w, 1350m, 1334m, 1300w, 1265w, 1224m, 1200s, 1172w, 1160w, 1140m,sh, 1027s, 1013s, 958m, 909w, 882s, 838w, 798m, 757w, 715m, 610w, 598w, 583w, 568w, 557w, 527w, 500w, and 472w  $\text{cm}^{-1}$ . An excess of powdered solid  $\text{CO}_2$  was added to a suspension of the substance (0.50 g) in diethyl ether (10 ml). The colour immediately changed from red to white. After stirring for 1 h, the mixture was hydrolysed with 2N- $\text{H}_2\text{SO}_4$ , extracted with diethyl ether (3 × 10 ml), and dried ( $\text{Na}_2\text{SO}_4$ ). Ether was evaporated and the residue was identified as 2,4,6-trimethylbenzoic acid by m.p. 147–149° (lit.,<sup>29</sup> 152°).

In a separate experiment, mesitylene (0.268 g, 0.00223 mol) was mixed with  $\text{Rb}_2\text{Et}_3\text{Be}_2(\text{OBu}^t)_3$  (0.240 g, 0.000485 mol) in a flask, on a vacuum-line, at –196°. The flask was allowed to warm to room temperature, then heated at

130–135° for 5 min. Ethane (0.000616 mol) was the only volatile substance formed.

*Lithium *t*-Butyl Bisdimethylamidoberyllate.*—*t*-Butyllithium (9.1 ml of a 1.2M pentane solution, 0.011 mol) was added to bisdimethylamidoberyllium (1.1 g, 0.0011 mol) in hexane (5 ml). After addition a white suspension formed, which was stirred for 2 h. The volatile material was evaporated and the residue crystallised from benzene (20 ml) as colourless prisms which decomposed on heating *ca.* 275° (Found: hydrolysable butyl, 35.1; Be, 5.4%.  $\text{C}_8\text{H}_{21}\text{BeLiN}_2$  requires hydrolysable butyl, 35.4; Be, 5.6%). The i.r. spectrum consists of absorptions at 2760s, 1248s, 1240m,sh, 1167m, 1140m, 1120s, 1093w, 1045s, 995m, 980w,sh, 950s, 825s, 810s, 753m, 715w, and 550s  $\text{cm}^{-1}$ .

*Bisdimethylamidoberyllium.*—*n*-Butyllithium (8.9 ml of 3.4M pentane solution, 0.030 mol) was added to dimethylamine (5 ml, an excess) in diethyl ether (50 ml) at –78°. After addition, the solution was warmed to room temperature and stirred for 1 h. Volatile matter was removed in vacuum and the pale yellow solid was exposed to vacuum for 2 h. To a diethyl ether (25 ml) suspension of lithium dimethylamide was added the bis(diethyl ether) complex of beryllium chloride (3.4 g, 0.015 mol) in diethyl ether (50 ml). After stirring for 1 h, solid was allowed to settle, ether was decanted, and solvent was removed in vacuum from the filtrate. The resulting pale yellow solid sublimed 95–100°, 10<sup>–2</sup> mmHg as white crystals, yield 0.69 g (45%), m.p. 88–92° (lit.,<sup>30</sup> 88–90°).

*Non-reaction of Sodium Hydride with Beryllium Di-*t*-butoxide (by Dr. N. A. Bell).*—Beryllium di-*t*-butoxide (0.70 g, 0.0045 mol) and sodium hydride (1.6 g, 0.065 mol) were boiled in refluxing 1,2-dimethoxyethane (150 ml) for 2 days. Hydrolysis of 5 ml of the clear solution yielded no hydrolysable hydrogen. Beryllium di-*t*-butoxide (1.3 g, 0.0083 mol) and sodium hydride (3.0 g, 0.13 mol) were boiled in refluxing tetrahydrofuran (100 ml) for 1 day. The tetrahydrofuran-insoluble matter was allowed to settle and hydrolysis of a 5 ml aliquot of the clear solution gave hydrolysable hydrogen (3.3 cm<sup>3</sup> at s.t.p.) and beryllium (0.0027 g), H:Be ratio 1.0:2.0. Soxhlet extraction of the solid material with tetrahydrofuran yielded a brown solution which was not further investigated as it is likely to be a decomposition product.

*With methylberyllium *t*-butoxide.* The alkoxide (0.82 g, 0.0085 mol) and sodium hydride (0.29 g, 0.012 mol) were stirred in diethyl ether (20 ml) for 12 h. Removal of solvent, addition of benzene, stirring, filtering, and removing benzene from the filtrate yielded a residue which crystallised as colourless plates from benzene-diethyl ether (5:2). When heated, it shrank *ca.* 90° and melted 185–195°. It was identified as  $(\text{MeBeOBu}^t)_4$  by its i.r. and  $^1\text{H}$  n.m.r. spectra.

*Non-reaction of Potassium Hydride with Di-*t*-butoxyberyllium.*—The alkoxide (0.70 g, 0.0045 mol) and the hydride (0.18 g, 0.0045 mol) were stirred in tetrahydrofuran (5 h). Hydrolysis of a 5 ml aliquot of clear solution yielded no hydrolysable hydrogen.

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<sup>29</sup> P. Jannasch and M. Weiler, *Chem. Ber.*, 1894, **27**, 3446.

<sup>30</sup> G. E. Coates and F. Glockling, *J. Chem. Soc.*, 1954, 22.