t-Butylberyllium-alkyls and -aryls: Amine Complexes and Pyrolysis to Hydrides

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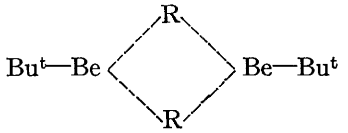
Dimethylberyllium dissolves in di-t-butylberyllium giving the liquid trimer $(Bu^tBeMe)_3$. Other t-butylberyllium alkyls and aryls prepared are the dimers $(Bu^tBeR)_2$, R = Et, *o*-tolyl, and *p*-xylyl. The cyclopentadienyl derivatives, C_5H_5BeR (R = Bu^t or C_6F_5), are monomeric. Pyrolysis of Bu^tBeR (R = Me, *o*-tolyl, and *m*-tolyl) yields the benzene-insoluble hydrides, RBeH, characterized as amine complexes.

The *NNN'N'*-tetramethylethylenediamine (tmed) complexes of Bu^tBeR (R = *o*- and *p*-tolyl or C_6F_5) are described. Other complexes prepared include $(Me_3SiCH_2)_2Be$,tmed, (*o*-tolyl)$_2$Be,quinuclidine, and the tetrahydrofuran complexes of di-t-butylberyllium and of bispentafluorophenylberyllium. t-Butylberyllium chloride is insoluble in benzene, but can be sublimed; its quinuclidine complex is insoluble in benzene.

SINCE the thermal elimination of isobutene from di-t-butylberyllium yields beryllium hydride[1] or, at lower temperatures, a mixture of iso- and tertiary-butylberyllium hydride,[2] pyrolysis of the t-butyl organoberyllium compounds Bu^tBeR (I) should provide a route to the synthesis of base-free organoberyllium hydrides, RBeH. Previously only one example of the latter has been described, namely isobutylberyllium hydride which was formed as a glassy material by the thermal decomposition of di-isobutylberyllium or of its diethyl ether complex.[2] To minimize complications it is desirable that the group R in (I) should itself be relatively thermally stable, *i.e.* it should be aromatic or, if aliphatic, should be methyl or should have no hydrogen attached to the carbon β to the beryllium. Compounds containing two different organic groups bound to beryllium have recently been described *viz.*, cyclopentadienyl(methyl)beryllium, C_5H_5BeMe,[3] and some amine complexes such as Me_3CCH_2BeMe,tmed (tmed = *NNN'N'*-tetramethylethylenediamine).[4]

There is no evidence that t-butyl groups can form electron-deficient bridges between beryllium atoms, Bu^t_2Be being monomeric,[5] so one might anticipate that t-butyl organoberyllium compounds (I) would be dimers (II) if the group R can form an electron-deficient bridge.



(II)

In fact, we report degrees of association of one, two, and three for various R groups in (I). Dimethylberyllium dissolves immediately in a solution containing an equimolar amount of di-t-butylberyllium in benzene:

$$3/n(Me_2Be)_n + 3Bu^t_2Be \longrightarrow 2(Bu^tBeMe)_3$$

The mixed alkyl (I; R = Me) is trimeric both in benzene and in cyclohexane solution. Unfortunately it is a liquid, and not a convenient subject for a crystal structure analysis. Noting that the metal atoms in (II) are only three-co-ordinate, one might tentatively speculate that some extra interactions, perhaps metal–metal, can take place in a trimer effectively raising the co-ordination number of the metal to four. The ^1H n.m.r. spectrum of $(Bu^tBeMe)_3$, in $[^2H_8]$toluene with benzene as reference, consists of a singlet at τ 8·99 due to t-butyl protons and a broad resonance centred on τ 10·09 due to methyl protons. The latter neither sharpened, nor split nor broadened as the temperature was reduced to −70°. To establish whether there is any substantial difference between the reactivities (*e.g.* to protic acids) of the butyl and methyl groups, the trimer was allowed to react at low temperature (warming from −196°) with three moles of t-butyl alcohol, *i.e.* one half of the amount needed for complete conversion to beryllium t-butoxide Butane and methane were formed in equimolar ratio. In an attempt to prepare an oligomer of dimethylberyllium chain-ended by t-butyl groups, dimethylberyllium was added to a solution of di-t-butylberyllium in benzene until solid dimethylberyllium remained

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[1] G. E. Coates and F. Glockling, *J. Chem. Soc.*, 1954, 2526; E. L. Head, C. E. Holley, and S. W. Rabideau, *J. Amer. Chem. Soc.*, 1957, **79**, 3687.

[2] G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1969, 1008.

[3] D. A. Drew and A. Haaland, *Chem. Comm.*, 1971, 1551; D. A. Drew and G. L. Morgan, unpublished observations.

[4] G. E. Coates and B. R. Francis, *J. Chem. Soc.* (*A*), 1971, 1305.

[5] G. E. Coates, P. D. Roberts, and A. J. Downs, *J. Chem. Soc.* (*A*), 1967, 1085.

undissolved after the mixture had been stirred overnight at ambient temperature. One mole of di-t-butylberyllium dissolved 2·2 mol of dimethylberyllium (reckoned as monomer), but attempted isolation of the product yielded only $(\mathrm{Bu^tBeMe})_3$ and dimethylberyllium. Since the latter is only very sparingly soluble in benzene, the solution must have contained a methyl-rich mixed alkyl before $(\mathrm{Bu^tBeMe})_3$ was separated by distillation.

Diethyl- and di-t-butyl-beryllium combine in 1 : 1 molar ratio giving $(\mathrm{Bu^tBeEt})_2$, and distillation yields no trace of the volatile $\mathrm{Bu^t{}_2Be}$, only the mixed alkyl which is very likely to have the constitution (II; R = Et). Dimethylberyllium is considerably more soluble in a solution of diethylberyllium in benzene than it is in benzene alone, and in one experiment in which equimolar amounts of the two were heated for 12 h in boiling benzene, the former dissolved until the methyl : ethyl ratio in the solution was *ca.* 0·4 : 1. Dimethylberyllium dissolved to a small extent in a boiling solution of dineopentylberyllium[6] in benzene, but cooling to room temperature resulted in crystallization of virtually all of the dimethylberyllium. Dimethylberyllium did not appear to dissolve in di-isobutylberyllium even at 80°.

Both diphenyl- and di-1-naphthyl-beryllium are very sparingly soluble in benzene and other hydrocarbon solvents, probably on account of good crystal packing or their association to polymeric species. Neither dissolves in a solution of di-t-butylberyllium, so we were unable to obtain the corresponding base-free arylberyllium hydrides by this route. Complexes of phenylberyllium hydride have previously been prepared.[7,8] The reduction of molecular symmetry resulting from the substitution of methyl groups in *ortho* or *meta* positions in the phenyl rings results in dimeric benzene-soluble beryllium di-aryls,[9] *e.g.* (*o*-tolyl)$_4$Be$_2$. We now find that di-*o*-tolyl- and di-*p*-xylyl-beryllium readily react with di-t-butylberyllium giving the (in benzene) dimers [Bu^{t}Be(*o*-tolyl)]$_2$ and [Bu^{t}Be(*p*-xylyl)]$_2$. Pyrolysis of the *o*-tolyl derivative in boiling xylene yields the insoluble *o*-tolylberyllium hydride. Even at room temperature, the reaction between di-*m*-tolylberyllium and di-t-butylberyllium results in an apparent mixture of Bu^{t}Be(*m*-tolyl) and (*m*-tolyl)BeH, but after heating at 140° the only product is the insoluble hydride. Both *o*- and *m*-tolylberyllium hydrides may be converted to soluble amine complexes, *e.g.* [(*o*-tolyl)BeH]$_2$tmed and [(*m*-tolyl)BeH,NMe$_3$]$_2$. The former can also be prepared from di-*o*-tolylberyllium, beryllium chloride, lithium hydride, and tmed,[8] and the latter was obtained from di-*m*-tolylberyllium by a similar method.

Pyrolysis of $(\mathrm{Bu^tBeMe})_3$ yields the benzene-insoluble methylberyllium hydride, which was converted to its trimethylamine complex for characterization. To our surprise, the m.p. of the product, whose i.r. and ^{1}H n.m.r. spectra were identical to those of methylberyllium hydride–trimethylamine prepared by other methods,[10] was 99—107° in contrast to the previously reported 73°. Therefore we examined again the hydride complex prepared from dimethylberyllium, beryllium bromide, lithium hydride, and trimethylamine, and found that the melting behaviour observed varies with the amount of material in the m.p. tube and with the rate of heating. We confirm that when a rather small sample (a few small crystals) is heated, it appears to melt at 72—73°, but slow heating of larger samples results in an impression of dampening (perhaps a phase transition) at 72—73°, and true melting then takes place in the range 99—107°. The relatively large melting range may be associated with *cis–trans* isomerization,[11] and the crystalline material may consist of one isomer only. Slow overnight sublimation at slightly above ambient temperature gave some relatively large (several mm long) crystals which melted at 109—112°. These observations remove the earlier anomaly that methylberyllium hydride–trimethylamine has a lower m.p. than its ethyl analogue (91°).

The pyrolysis of $(\mathrm{Bu^tBeEt})_2$ could be complicated by the decomposition of both kinds of alkyl group. However, heating a mixture of the mixed alkyl with diethylberyllium gives the hydride $\mathrm{Et_3Be_2H}$, identical with the product described previously.[6]

$$(\mathrm{Bu^tBeEt})_2 + 2\mathrm{Et_2Be} \longrightarrow 2\mathrm{Et_3Be_2H} + 2\mathrm{C_4H_8}$$

Biscyclopentadienylberyllium reacts with di-t-butylberyllium (either base-free or the diethyl ether complex) giving the volatile monomeric $\mathrm{Bu^tBeC_5H_5}$, analogous to $\mathrm{MeBeC_5H_5}$,[3] which gives no complex with tmed nor with quinuclidine. It is sensitive to protonic acids and reaction with t-butyl alcohol yields $[\mathrm{Be(OBu^t)_2}]_3$.[12] Remarkably, reaction with only one mole of t-butyl alcohol gives the same product:

$$2\mathrm{Bu^tBeC_5H_5} + 2\mathrm{Bu^tOH} = \mathrm{Bu^tBeC_5H_5} + 1/3[\mathrm{Be(OBu^t)_2}]_3 + \mathrm{C_5H_6} + \mathrm{C_4H_{10}}$$

Biscyclopentadienylberyllium also reacts with $(\mathrm{C_6F_5})_2\mathrm{Be(thf)_2}$ (thf = tetrahydrofuran) giving monomeric $\mathrm{C_6F_5BeC_5H_5}$, which is the first base-free pentafluorophenylberyllium compound to be prepared. Surprisingly, biscyclopentadienylberyllium was recovered unchanged from its mixtures with $(\mathrm{Bu^tCH_2})_2\mathrm{Be}$ and with $(\mathrm{Me_3SiCH_2})_2\mathrm{Be}$ even after the mixtures had remained 60 and 24 h respectively at room temperature.

Di-t-butylberyllium reacts with a suspension of beryllium chloride in benzene, giving a benzene-insoluble product of composition close to that of t-butylberyllium chloride. This material had a melting point of 123—124° (decomp.). However, after sublimation the compound appeared to soften at *ca.* 125° but did not melt

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[6] G. E. Coates and B. R. Francis, *J. Chem. Soc.* (*A*), **1971**, 1308.

[7] G. E. Coates and M. Tranah, *J. Chem. Soc.* (*A*), **1967**, 236.

[8] U. Blindheim, G. E. Coates, and R. C. Srivastava, *J.C.S. Dalton*, **1972**, 2302.

[9] G. E. Coates and R. C. Srivastava, *J.C.S. Dalton*, **1972**, 1541.

[10] N. A. Bell and G. E. Coates, *J. Chem. Soc.*, **1965**, 692.

[11] N. A. Bell, G. E. Coates, and J. W. Emsley, *J. Chem. Soc.* (*A*), **1966**, 1360.

[12] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), **1968**, 823.

up to 320°; the composition of the sublimate, as found by analysis, was the same as that of the material which melted at 123—124°. The quinuclidine complex of t-butylberyllium chloride is insoluble in benzene.

The preparations of several co-ordination complexes of organoberyllium compounds, RBeR' and R_2Be, are described in the Experimental section. These call for little comment, but it is noteworthy that the tmed complex of $Bu^tBeC_6H_5$ was not obtained by a procedure analogous to that which afforded $Bu^tBeC_6F_5$,tmed; instead the main product was Ph_2Be,tmed. The complexes (*o*-tolyl)$_2$Be,quinuclidine and Bu^t_2Be,thf are both monomeric in benzene and hence provide further examples of three-co-ordinate beryllium. An attempt to obtain $EtBeC_6F_5$ or EtBeF by reaction between Et_2Be and C_6F_5H failed, since no reaction took place after an hour in boiling benzene: diethylberyllium was recovered from the reaction mixture.

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, usually beginning with 2-methoxyethanol at low temperature, followed by quantitative separation and measurement of volatile material and volumetric determination of beryllium by the fluoride method[13] under standardized conditions. Molecular weights were, unless stated otherwise, determined cryoscopically in benzene. Most of the compounds described below are very sensitive to air and water, and to minimize the number of transfers from one vessel to another, *e.g.* for weighing, yields were not recorded. Except for transfer and recrystallization losses yields appeared to be nearly quantitative. ^1H N.m.r. spectra were recorded by use of a Varian HA100 spectrometer, with benzene as solvent and internal reference unless otherwise stated.

t-Butyl(methyl)beryllium, $(Bu^tBeMe)_3$.—Dimethylberyllium (0·71 g, 0·0182 mol) was dissolved in a solution of di-t-butylberyllium (2·3 g, 0·0187 mol) in benzene (5 ml), After evaporation of all volatile material under pressure, the residue was distilled, b.p. 32°, 10^{-3} mmHg [Found: Be, 11·4; hydrolysable methyl, 18·4; hydrolysable butyl, 71·6%; *M* (cryoscopically, 0·78 wt.% in cyclohexane and 1·42 wt.% in benzene) 232 and 245. $C_{15}H_{36}Be_3$ requires Be, 11·1; hydrolysable methyl, 18·5; hydrolysable butyl, 70·3%; *M*, 243].

Reaction of t-Butyl(methyl)beryllium with Bases.—(*a*) *With diethyl ether.* Addition of the ether (2 ml) to $(Bu^tBeMe)_3$ (1·1 g) at room temperature resulted in appreciable warming. After evaporation of the excess of ether the residue was distilled at room temperature (10^{-3} mmHg) giving a colourless liquid adduct, analysis of which gave the Be : Me : Bu^t : Et_2O ratio as 1 : 0·98 : 1·01 : 0·58.

(*b*) *With tetramethylethylenediamine.* The diamine (1·40 g) was added to $(Bu^tBeMe)_3$ (0·91 g) in benzene (5 ml). The liquid *adduct* remained after volatile material had been evaporated under reduced pressure (Found: Be, 4·9; hydrolysable methyl, 8·0; hydrolysable butyl, 30·0%. $C_{11}H_{28}BeN_2$ requires Be, 4·6; hydrolysable methyl, 7·6; hydrolysable butyl, 28·9%).

(*c*) *With trimethylamine.* The amine in excess was condensed on the beryllium alkyl, and after evaporation of volatile matter the residue was distilled (10^{-3} mmHg) at a little above room temperature. The ^1H n.m.r. spectrum of the product consisted of singlets at τ 10·13 (CH_3Be), 9·06 $C(CH_3)_3$, and 8·13 (CH_3N) in area ratio 3 : 10 : 5.

t-Butyl(ethyl)beryllium, $(Bu^tBeEt)_2$.—A mixture of diethylberyllium (0·60 g, 0·009 mol as monomer) and di-t-butylberyllium (1·12 g, 0·0091 mol) was stirred 12 h and then distilled at 60—65°, 10^{-3} mmHg giving the colourless *dimer* [Found: Be, 9·4; hydrolysable ethyl, 29·0; hydrolysable butyl, 61·0%; *M* (0·64 and 0·94 wt.%) 180, and 202. $C_{12}H_{28}Be_2$ requires Be, 9·5; hydrolysable ethyl, 30·3; hydrolysable butyl, 60·0%, *M*, 190].

t-Butyl(o-tolyl)beryllium.—After a mixture of di-t-butylberyllium (0·74 g, 0·0060 mol) and di-*o*-tolylberyllium[9] (1·15 g, 0·0060 mol as monomer) in benzene (10 ml) had been stirred 12 h, solvent was removed by evaporation and the residue was crystallized from hexane (at 5—6°) as *prisms*, m.p. 135° (decomp.) [Found: Be, 5·80; hydrolysable butyl, 36·5; hydrolysable tolyl, 57·85%; *M* (0·85 and 1·28 wt.%) 310 and 318. $C_{22}H_{32}Be_2$ requires Be, 5·7; hydrolysable butyl, 36·3; hydrolysable tolyl, 58·0%, *M*, 314].

t-Butyl(p-*xylyl*)*beryllium.*—This was similarly prepared, from di-*p*-xylylberyllium,[9] and crystallized from hexane–benzene (10 : 1) as *prisms*, m.p. 139—141° (decomp.) [Found: Be, 5·3; hydrolysable butyl, 33·0; hydrolysable xylyl, 61·8%; *M* (0·68 and 1·02 wt.%) 338 and 344. $C_{24}H_{36}Be_2$ requires Be, 5·3; hydrolysable butyl, 33·3; hydrolysable xylyl, 61·4%; *M*, 342].

Organoberyllium Hydrides, Methylberyllium Hydride.—t-Butyl(methyl)beryllium (0·50 g) was heated at 150° for 2 h in a nitrogen atmosphere, and then at 120° at 10^{-3} mmHg for 10 h. During the latter period a trace of dimethylberyllium sublimed and was identified by its i.r. spectrum. The residual white benzene-insoluble solid (0·15 g) had an i.r. absorption centred at 1800 cm^{-1} (width at half height *ca.* 200 cm^{-1}). Trimethylamine in excess was condensed (liquid N_2) on this product, and after removal of the excess of amine the residue was sublimed at 70°, 10^{-3} mmHg, and then had m.p. 104—107° (Found: Be, 10·8; Me_3N, 69·5%; $CH_4 + H_2$, 13·5 c.c. at s.t.p. from 51 mg of complex. Calc. for $C_4H_{13}BeN$: Be, 10·7; Me_3N, 70·2%; $CH_4 + H_2$, 13·6 c.c. at s.t.p.).

o-*Tolylberyllium Hydride.*—When t-butyl(*o*-tolyl)beryllium was heated in boiling xylene for 24 h a white precipitate appeared, which was insoluble also in boiling benzene (Found: Be, 9·3; hydrolysable hydride, 0·90; hydrolysable tolyl, 89·5%. C_7H_8Be requires Be, 8·9; hydrolysable hydride, 1·0; hydrolysable tolyl, 90·1%). Reaction of this product with tmed gave a complex identical (i.r. spectrum) with that prepared from di-*o*-tolylberyllium, beryllium chloride, lithium hydride, and tmed.[8]

m-*Tolylberyllium Hydride.*—Di-*m*-tolylberyllium (0·70 g) and di-t-butylberyllium (0·45 g) were stirred in benzene (5 ml) for 24 h. The solid residue, left after volatile material had been evaporated, was heated at 140°, 10^{-3} mmHg for 24 h, and gave the *hydride* (Found: Be, 9·2; hydrolysable hydride, 0·90; hydrolysable tolyl, 89·6%. C_7H_8Be requires Be, 8·9; hydrolysable hydride, 1·0; hydrolysable tolyl, 90·1%). The hydride assumed a glassy appearance at *ca.* 200° and decomposed at *ca.* 260°.

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[13] D. A. Everest, 'The Chemistry of Beryllium,' Elsevier, Amsterdam, 1964, p. 120.

m-*Tolylberyllium Hydride–Trimethylamine*.—This was obtained by addition of the amine in excess to the hydride and subsequent removal of the excess of amine. It had m.p. 165—167° and an i.r. spectrum identical with that of the same complex prepared as follows. Di-*m*-tolylberyllium (0·76 g), beryllium chloride–bisdiethyl ether (0·91 g), and lithium hydride (0·080 g) were stirred in boiling diethyl ether (15 ml) for 30 h. After the ether had been evaporated, benzene (10 ml) was added and lithium chloride was separated. Trimethylamine in excess was condensed on the filtrate, which had been cooled in liquid nitrogen. After the mixture had warmed to room temperature and been stirred for ½ h, volatile material was evaporated under reduced pressure and the residue was crystallized from benzene–hexane as *needles*, m.p. 168—169° [Found: Be, 5·7; hydrolysable hydride, 0·60; hydrolysable tolyl, 55·6%, *M* (0·58 and 0·87 wt.%) 328 and 322. $C_{20}H_{34}Be_2N_2$ requires Be, 5·6; hydrolysable hydride, 0·60; hydrolysable tolyl, 56·9%; *M*, 320]. The ^1H n.m.r. spectrum consisted of singlets at τ 7·41 and 7·99 in area ratio 1 : 3 due to C–CH_3 and N–CH_3 respectively. The resonance due to the hydridic protons was, as usual, not observed.

Triethyldiberyllium Hydride, Et_3Be_2H.—Diethylberyllium (0·20 g) mixed with t-butyl(ethyl)beryllium (0·28 g) was set aside for a week and was then heated (140°) for 1 h. The colourless solid which was deposited as the mixture cooled to room temperature was washed with benzene, and had m.p. 132—134° (lit.[6] 133—136°). It had the same i.r. spectrum as that of the previously prepared hydride.

t-Butyl(cyclopentadienyl)beryllium.—Biscyclopentadienylberyllium (1·52 g, 0·0011 mol) and di-t-butylberyllium (1·35 g, 0·0011 mol) in benzene (5 ml) were stirred overnight, after which removal of solvent left the crystalline *product*, m.p. 39—40° [Found: Be, 6·9; hydrolysable butyl, 43·3; hydrolysable cyclopentadienyl, 49·5%; *M* (0·66 and 0·99 wt.%) 134 and 138. $C_9H_{14}Be$ requires Be, 6·9; hydrolysable butyl, 43·5; hydrolysable cyclopentadienyl, 49·6%; *M*, 131]. The product is so volatile that some of it was lost on evaporation of the benzene.

Reaction with t-Butyl Alcohol.—The alcohol (0·20 g, 0·0027 mol) was added to t-butyl(cyclopentadienyl)beryllium (0·36 g, 0·0027 mol) in pentane (5 ml) at −40°. After the mixture had warmed to toom temperature, volatile matter, including unreacted t-butyl(cyclopentadienyl)beryllium, was removed, leaving beryllium t-butoxide, m.p. 113—114° (lit.[12] 112°), identified also by its i.r. spectrum.

t-Butyl(pentafluorophenyl)beryllium.—After a solution of biscyclopentadienylberyllium (0·21 g., 0·0015 mol) and the bistetrahydrofuran complex of bispentafluorophenylberyllium (0·73 g, 0·0015 mol) in benzene (2 ml) had been set aside 30 h, volatile material was removed by evaporation, and the residue was sublimed at 100°, 10^{-4} mmHg. The sublimed *product* had m.p. 108—109° (decomp.) [Found: Be, 3·7; hydrolysable cyclopentadienyl, 26·8; hydrolysable pentafluorophenyl, 68·9%, *M* (0·56 and 0·84 wt.%) 252 and 248. $C_{11}H_5BeF_5$ requires Be, 3·7; hydrolysable cyclopentadienyl, 27·0; hydrolysable pentafluorophenyl, 69·3%; *M*, 241].

t-Butylberyllium Chloride.—Beryllium chloride (sublimed powder, 0·48 g, 0·0060 mol) was stirred 24 h in suspension in a solution of di-t-butylberyllium (0·75 g, 0·0061 mol). After solvent had been removed, finally at 10^{-3} mmHg, the residual solid was washed with benzene and adhering solvent removed under reduced pressure, m.p. 123—124° (decomp.) (Found: Be 9·2; hydrolysable butyl, 54·9%. C_4H_9BeCl requires Be, 8·9; Cl, 35·0; hydrolysable butyl, 56·1%). Part of this product was sublimed at 120—130°, 10^{-3} mmHg. The sublimate (*ca.* 70—80% of the sample taken) softened at about 125° and did not melt up to 320° (Found: Be, 9·1; Cl, 34·8; hydrolysable butyl, 55·0%. C_4H_9BeCl requires Be, 8·9; Cl, 35·0; hydrolysable butyl, 56·1%).

t-Butylberyllium Chloride–Quinuclidine.—The amine (1 g, an excess) was added to a suspension of unsublimed t-butylberyllium chloride, resulting in perceptible heat evolution. After the suspension had been stirred ½ h, the solid product was separated, washed with warm benzene and dried, m.p. decomposed above 200° (Found: Be, 4·4; hydrolysable butyl, 26·0%. $C_{11}H_{22}BeClN$ requires Be, 4·2; hydrolysable butyl, 26·8%).

Complexes of t-Butylberyllium Aryls with NNN′N′-*Tetramethylethylenediamine*.—(*a*) Bu^tBe(o-*tolyl*)*tmed*. The diamine (1 ml, an excess) was added (heat evolution) to t-butyl-*o*-tolylberyllium (0·54 g) in benzene (5 ml). After 15 min volatile material was removed under reduced pressure and the residue was recrystallized from hexane as *prisms*, m.p. 90—92° [Found: Be, 3·4; hydrolysable butyl, 20·7; hydrolysable tolyl, 33·0%, *M* (0·56 and 0·84 wt.%) 270 and 277. $C_{17}H_{32}BeN_2$ requires Be, 3·3; hydrolysable butyl, 20·9; hydrolysable tolyl, 33·3%; *M*, 273].

(*b*) Bu^tBe(p-*xylyl*)*tmed*. This was similarly prepared and crystallized from benzene–hexane (1 : 10) as *prisms*, m.p. 105—107° [Found: Be, 3·0; hydrolysable butyl, 19·8; hydrolysable xylyl, 36·1%; *M* (0·86 and 1·29 wt.%) 290 and 286. $C_{18}H_{34}BeN_2$ requires Be, 3·1; hydrolysable butyl, 19·9; hydrolysable xylyl, 36·6%; *M*, 287].

(*c*) $Bu^tBeC_6F_5$,*tmed*. Di-t-butylberyllium diethyl ether complex (0·41 g) and $(C_6F_5)_2Be,0{\cdot}7Et_2O$[9] (0·83 g) were dissolved in benzene (4 ml). After two days the diamine (1 ml, an excess) was added and after ½ h volatile material was evaporated under reduced pressure and the residue was recrystallized from benzene–hexane as *prisms*, m.p. 95—98° (decomp.), which decompose slowly at room temperature [Found: Be, 2·5; hydrolysable butyl, 16·3; hydrolysable pentafluorophenyl, 47·2%; *M* (0·74 and 1·11 wt.%) 360 and 365. $C_{16}H_{25}BeF_5N_2$ requires Be, 2·6; hydrolysable butyl, 16·3; hydrolysable pentafluorophenyl, 47·8$_5$%; *M*, 349].

Complexes of Beryllium Dialkyls and Diaryls

Di-t-butylberyllium–Tetrahydrofuran, Bu^t_2Be,thf.—This was prepared from t-butylmagnesium chloride and beryllium chloride in diethyl ether. After removal of most of the ether, tetrahydrofuran was added. After decantation from magnesium chloride, the tetrahydrofuran solution was distilled, finally under reduced pressure. The distillate solidified at room temperature, m.p. 36° [Found: Be, 4·55; hydrolysable butyl, 58·3%; *M* (0·58 and 0·89 wt.%) 200 and 206. $C_{12}H_{26}BeO$ requires Be, 4·6; hydrolysable butyl, 58·5%; *M*, 195]. The complex can be sublimed at 25—30°, 10^{-3} mmHg.

Bistrimethylsilylmethylberyllium,tmed Complex.—This was obtained from the diamine (a slight excess) and the beryllium dialkyl[6] in benzene. After evaporation of solvent the residue was recrystallized from hexane, m.p. 96—97° [Found: Be, 3·1; hydrolysable trimethylsilylmethyl (as Me_4Si), 58·0%; *M* (0·66 and 0·99 wt.%) 304 and 295. $C_{14}H_{38}BeN_2Si_2$ requires Be, 3·0; hydrolysable trimethylsilylmethyl, 58·2%, *M*, 299].

Di-o-tolylberyllium–Quinuclidine (o-tolyl)$_2BeNC_7H_{13}$.—

The amine (0·26 g, 0·00234 mol) in benzene (5 ml) was added to di-*o*-tolylberyllium (0·42 g, 0·0022 mol) in benzene (2 ml). After evaporation of the benzene, the residue was recrystallized from benzene–hexane as *needles*, m.p. 220—222° [Found: Be, 3·0; hydrolysable tolyl, 59·3%; *M* (0·66 and 0·99 wt.%) 300 and 310. $C_{21}H_{27}BeN$ requires Be, 3·0; hydrolysable tolyl, 60·3%; *M*, 302].

Bispentafluorophenylberyllium Bistetrahydrofuran, $(C_6F_5)_2$-Be(thf)$_2$.—Addition of tetrahydrofuran to a solution of bispentafluorophenylberyllium in ether resulted in a mildly exothermic reaction. After concentration, the complex crystallized as *needles*, m.p. 134—136° [Found: Be, 1·80; hydrolysable pentafluorophenyl, 68·4%; *M* (0·48 and 0·72 wt.%) 475 and 480. $C_{20}H_{16}BeF_{10}O_2$ requires Be, 1·85; hydrolysable pentafluorophenyl, 68·6%; *M*, 487].

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