Reactions of Beryllium Alkyls with Carbonyl and Azomethine Groups: Addition, Reduction, Complex Formation, and *ortho*-Metallation

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Reaction of beryllium alkyls with ketones and aldehydes yields compounds of the type $RBeOCHR'_2$ and $RBeOCH_2R'$ respectively, where R is Et, Bu^i, Bu^t, and R′ is Bu^t and Ph. These alkoxides are all dimeric except $Bu^iBeOCH_2Bu^t$ which is trimeric. t-Butylberyllium chloride gives $(ClBeOCHBu^t_2)_2$ and $(ClBeOCH_2Bu^t,OEt_2)_{1-2}$ respectively. The latter readily loses ether *in vacuo* giving benzene-insoluble $ClBeOCH_2Bu^t$, and reacts with *NNN′N′*-tetramethylethylenediamine (tmed) giving $(ClBeOCH_2Bu^t)_2$(tmed). These reductions proceed *via* a yellow or orange colour at −78°, except for benzophenone (purple), likely due to formation of a π-complex between the carbonyl group and the beryllium alkyl during or prior to hydride transfer. Dimethylberyllium adds to Bu^t_2CO, and $(Me_3SiCH_2)_2Be$ adds to Ph_2CO giving $(MeBeOCMeBu^t_2)_2$ and $(Me_3SiCH_2BeOCPh_2CH_2SiMe_3)_2$ respectively, the latter by way of a red colour at −78°. Diphenylberyllium and $(Me_3SiCH_2)_2Be$ give colourless co-ordination complexes with Ph_2CO, $Ph_2CO \longrightarrow BeR_2$. In contrast to the rapid reduction of aldehydes and ketones only a few azomethines and no alkyl cyanides are reduced, addition and complex formation being observed. Di-t-butylberyllium reduces PhCH=NMe and PhCH=CHCH=NPh giving dimeric $[Bu^tBeN(Me)CH_2Ph]_2$ and $[Bu^tBeN(Ph)CH_2CH{=}CHPh]_2$ respectively though it forms a red complex with benzylideneaniline, $Bu^t_2Be,N(Ph){=}CHPh$. Diphenylberyllium gives a tan complex with PhCH=N(*p*-tolyl) though a colourless one with PhCH=NMe. The colourless complexes $Me_2Be,N(Me){=}CHPh$, $Bu^t_2Be,N(Me){=}CHPr^i$, $Bu^tBeCl,NCBu^t$ were also prepared. Diethylberyllium adds across the C=N in PhCH=NMe and PhCH=NPh yielding $[EtBeN(Me)CHEtPh_2]$ and $[EtBeN(Ph)CHEtPh]_2$. Dimethylberyllium gives the benzene-insoluble alkylation product, MeBeN(Ph)CHMePh, with the latter azomethine though the *p*-toluidine derivative is a dimer. Reaction of $PhCH{=}NBu^t$ with Et_2Be gives the yellow dimeric *ortho*-metallation product ethyl-2-(*N*-t-butylformimidoylphenyl)beryllium. The t-butyl analogue has a degree of association between 1 and 2.

SINCE the discovery [1] in 1937 that triethylaluminium and triethylborane both reduce chloral with elimination of ethylene, similar reductions of carbonyl and other unsaturated groups have been found to occur with triisobutylaluminium [2] and the preparative value of these reactions has been critically reviewed.[3] Some alkyls of second group elements react in a similar way, *e.g.* diethylzinc quantitatively reduces benzophenone [4] and the reduction of 2,2,4,4-tetramethylpentan-3-one (di-t-butyl ketone) by di-t-butylmagnesium has been studied in detail.[5] We report here a brief examination of reactions, mainly of di-t-butylberyllium, with a few ketones, azomethines, and cyanides. Earlier it had been reported that methylberyllium hydride in ether rapidly reduces benzaldehyde, benzophenone, and *N*-benzylideneaniline.[6]

Addition of Be–C across a carbonyl bond was the only reaction observed between benzophenone and either diphenyl- or bistrimethylsilylmethyl-beryllium, giving $(PhBeOCPh_3)_2$ and $(Me_3SiCH_2BeOCPh_2CH_2SiMe_3)_2$. The former reaction was carried out in benzene, and was quantitative, in contrast to the recovery of 34% of the benzophenone previously observed when the reaction took place in diethyl ether.[7] Phenylberyllium triphenylmethoxide is remarkably resistant to hydrolysis, doubtless on account of steric obstruction of the attacking reagent, as found in the case of dialkylaluminium

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[1] H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.*, 1937, **147**, 226.

[2] K. Ziegler, K. Schneider, and J. Schneider, *Annalen*, 1959, **623**, 9.

[3] G. Bruno, 'The Use of Aluminium Alkyls in Organic Synthesis,' Ethyl Corporation, Industrial Chemical Division, Baton Rouge, Louisiana, 1970; Supplement 1973.

[4] G. E. Coates and D. Ridley, *J. Chem. Soc.* (*A*), 1966, 1064.

[5] M. S. Singer, R. M. Salinger, and H. S. Mosher, *J. Org. Chem.*, 1967, **32**, 3821.

[6] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.

[7] G. Wittig, F. J. Meyer, and G. Lange, *Annalen*, 1951, **571**, 167.

tertiary alkoxides.[8] Phenylberyllium triphenylmethoxide dissolves neither in 1M-sulphuric nor in 6M-nitric acid at room temperature, but reacts with acid when the alkoxide is in ether solution. t-Butylberyllium triphenylmethoxide, $(Bu^tBeOCPh_3)_2$, is hydrolysed much more readily than its phenylberyllium analogue. Though $(PhBeOCPh_3)_2$ and $(Me_3SiCH_2BeOCPh_2CH_2SiMe_3)_2$ are colourless, as expected, the addition of benzophenone to diphenylberyllium suspended in benzene results in a deep yellow solution which fades to a very pale yellow colour in a few minutes. Similarly, the addition of benzophenone to $(Me_3SiCH_2)_2Be$ in benzene results in a deep red colour which rapidly fades. Colours, which must be due to reaction intermediates, were also observed in all of the reactions in which carbonyl groups were reduced. These colours are not necessarily due to normal *sigma*-type co-ordination complexes, such as $Ph_2CO \longrightarrow BePh_2$, since in two instances, $Bu^t_2CO \longrightarrow BePh_2$ and $Bu^t_2CO \longrightarrow Be(CH_2SiMe_3)_2$, the complexes could be isolated and both are colourless. However, we also obtained some co-ordination complexes from beryllium alkyls and azomethines: some are colourless, two are coloured, and in another case there was a transient coloured reaction intermediate. Quinuclidine (1-azabicyclo[2.2.2]octane), which is a very strong base, displaces di-t-butyl ketone from its diphenylberyllium complex, giving the bisquinuclidine complex of diphenylberyllium. Dimethylberyllium adds to di-t-butyl ketone in diethyl ether giving $(MeBeOCMeBu^t_2)_2$, and this is the only reaction of beryllium alkyls reported here, other than the formation of some of the colourless co-ordination complexes and reactions with protic acids, in which no coloured intermediate was apparent.

In all of the reactions discussed above there is no possibility of reduction and olefin formation, adduct formation or addition of Be–C across the carbonyl group being the only reactions possible. As mentioned earlier, reduction of carbonyl compounds by metal alkyls capable of olefin elimination have been extensively studied, and, for example, Mole and Surtees[9] found that whereas Me_3Al methylated benzophenone, Et_3Al both reduced and alkylated, whereas Bu^i_3Al only reduced it. These authors also noted the colours (yellow to red) of transient reaction intermediates. Of the numerous beryllium alkyls capable of acting as reducing agents with olefin elimination, we have experimented only with Et_2Be, Bu^i_2Be, and Bu^t_2Be. In two experiments only, *viz.* the reaction of Et_2Be with Bu^tCHO and with Ph_2CO in hexane, did we obtain evidence for alkylation proceeding competitively with reduction, and from measurement (vacuum-line) of evolved ethylene, reduction accounted for 78 and 42% respectively of the overall reactions. In all other instances, reduction was the only reaction observed. Different results (see below) were obtained with azomethines since in several instances we obtained co-ordination complexes even with Bu^t_2Be.

With one exception we used only aldehydes and ketones that were unable to enolise, to avoid complications that accompany enolisation and consequent alkane formation.

Di-t-butyl ketone is reduced rapidly by two moles of di-t-butylberyllium giving the alkoxide $(Bu^t_2CHO)_2Be$ which is too sparingly soluble in benzene to allow measurements of its molecular weight by methods currently available to us. The same compound was prepared from the alcohol Bu^t_2CHOH and diethylberyllium. Since only beryllium tertiary alkoxides, and other highly hindered alkoxides such as beryllium 2,6-di-t-butylphenoxide[10] are mono- or oligo-meric, the low solubility of $(Bu^t_2CHO)_2Be$ is not surprising. However, $(Bu^t_2EtCO)_2Be$, which we obtained from the alcohol, Bu^t_2EtCOH, and diethylberyllium is also sparingly soluble. This is surprising in view of the high solubility of alkoxides such as $[Be(OCEt_3)_2]_2$.[11]

The reaction of di-t-butyl ketone with one mole of di-t-butylberyllium results in a bright yellow solution (ether, −78°) which fades as it warms, yielding the reduction product $(Bu^tBeOCHBu^t_2)_2$. Since the appearance of colour in a relatively simple system containing neither transition metal atoms nor aromatic compounds was so surprising, we investigated the possibility that the colour might be due to an intermediate complex $Bu^t_2CO \longrightarrow BeBu^t_2$. However, addition of *NNN′N′*-tetramethylethylenediamine (tmed) to the reaction mixture at −78° had no perceptible effect on the colour. Addition of di-t-butyl ketone to di-t-butylberyllium in ether at −78° resulted in a yellow colour, as previously observed, but this was not altered by the addition of quinuclidine. The colour faded as previously observed when the mixture warmed to room temperature, but the product isolated was then the colourless monomeric complex $Bu^tBeOCHBu^t_2,C_7H_{13}N$. The same yellow colour was evident when di-t-butyl ketone was added to a solution of the di-t-butylberyllium complex with quinuclidine in ether at −78°, and again the product was the colourless quinuclidine complex. It seems unlikely that a ketone would be able to displace quinuclidine from di-t-butylberyllium. We offer only as a tentative suggestion that light absorption causes an electron transfer from the two beryllium–carbon bonds to the π^* orbital of the ketone, possibly as a π-complex with R_2Be, and that as the ketone is reduced to an alkoxide this possibility disappears (along with the colour). The intermediacy of a π-complex has recently been suggested from kinetic studies of addition of Me_3Al to Ph_2CO.[12] Similarly addition of di-t-butyl ketone to the Bu^t_2Be(tmed) complex results in a yellow colour and formation of the colourless alkoxide $(Bu^tBeOCHBu^t_2)_2$. The latter is attacked by 4-dimethylaminopyridine giving monomeric $Bu^tBeOCHBu^t_2,NC_5H_4NMe_2$. It may be noted at this point that 4-dimethylaminopyridine

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[8] E. G. Hoffmann and W. Tornau, *Angew. Chem.*, 1961, **73**, 578.

[9] T. Mole and J. R. Surtees, *Austral. J. Chem.*, 1964, **17**, 961.

[10] R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1972, 2153.

[11] G. E. Coates and A. H. Fishwick, *J. Chem. Soc. (A)*, 1968, 477.

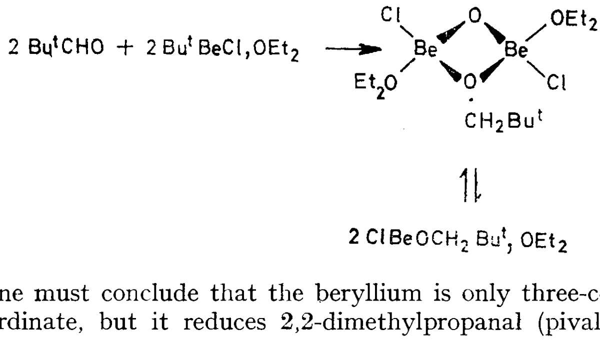
[12] H. M. Neumann, J. Laemmle, and E. C. Ashby, *J. Amer. Chem. Soc.*, 1973, **95**, 2597.

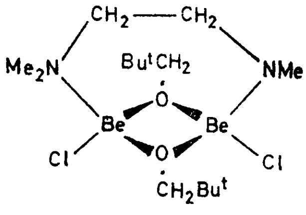
appears to behave as a stronger base relative to beryllium di-t-butoxide even than quinuclidine, since the former depolymerises the butoxide[10] and the latter does not. 4-Dimethylaminopyridine was not used in experiments involving reduction by di-t-butylberyllium on account of the complications which might result from the reduction of the pyridine ring.

Di-t-butylberyllium and benzophenone give a deep violet solution in diethyl ether (−78°) which fades to colourless as it warms, yielding the reduction product $(Bu^tBeOCHPh_2)_2$. The alkoxide will not eliminate isobutene on heating in decalin (180°, 3 h). That di-t-butylberyllium and diphenylmethanol give $(Bu^tBeOCHPh_2)_2$ without the development of a violet or other colour (ether, −78°) further supports the suggestion of a π-system with regard to transient colours. We feel the charge transfer is most reasonably considered to be from the Be–C bond to the antibonding molecular orbital of the ketone for the following reasons. The diphenylberyllium–bipyridyl complex is pale yellow, whereas Et_2Be,bipy is red,[13] the most reasonable explanation being charge transfer from a Be–C bond into the lowest unoccupied molecular orbital of the aromatic ring. Since the colour developed in the $Ph_2Be + Ph_2CO$ reaction is yellow and that in the $Bu^t_2Be + Ph_2CO$ reaction is violet, this parallels that found in the bipyridyl situation, *i.e.* $Be–C_{aryl}$ bonds give transitions of lower energy than that by $Be–C_{alkyl}$, aryl groups being electron withdrawing relative to alkyl groups. This strongly suggests that the electron-transfer processes involved are similar, *i.e.*, from R_2Be to R_2CO. Also electron transfer *to* an electropositive metal–carbon bond is likely to be rather unfavourable relative to electron transfer from it.

Di-t-butyl ketone is rapidly reduced by diethylberyllium giving $(EtBeOCHBu^t_2)_2$, and in a supplementary experiment in which evolved ethylene was measured (vacuum line) the reduction was found to be quantitative. As expected, it is also reduced by di-isobutylberyllium, giving $(Bu^iBeOCHBu^t_2)_2$ which does not itself reduce any more ketone (contrast $Bu^tBeOCHBu^t_2$ and $Bu^iBeOCH_2Bu^t$).

t-Butylberyllium chloride (in ether) reduces di-t-butyl ketone giving ether-free $(ClBeOCHBu^t_2)_2$ in which one must conclude that the beryllium is only three-co-ordinate, but it reduces 2,2-dimethylpropanal (pivalic aldehyde) giving an ether complex. The latter has an apparent degree of association between 1·4 and 1·7, in benzene, consistent with the above equilibrium. Support for the proposed equilibrium is found by quantitative removal of diethyl ether on exposure of the complex to vacuum, giving benzene-insoluble $(ClBeOCH_2Bu^t)_x$. Reaction with tmed gives the complex $(ClBeOCH_2Bu^t)_2$(tmed), which could well have the structure (I).





(I)

The only trimeric as well as the only liquid alkylberyllium alkoxide prepared in this study, $(Bu^iBeOCH_2Bu^t)_3$, from pivalic aldehyde and di-i-butylberyllium, reacts with further aldehyde giving the insoluble $(Bu^tCH_2O)_2Be$ described above. In contrast Bu^t_2Be and pivalic aldehyde give dimeric $(Bu^tBeOCHBu^t_2)_2$.

Reaction of acetone and the diethyl ether complex of di-t-butylberyllium gives $(Bu^tBeOPr^i)_2$. Since acetone can enolise, we measured the volatile materials (vacuum-line) formed. Only isobutene and diethyl ether were found, so enolisation does not present any problem in this instance.

In only one case did we find a diorganoberyllium compound inert to a carbonyl compound. Cyclopentadienyl-t-butylberyllium was quantitatively recovered after mixing with 2,2,4,4-tetramethylpentan-3-one. Though dimethylzinc does not add to benzophenone, a yellow colour is observed on mixing.[4] In the case of the cyclopentadienyl compound no colour was visible.

Reaction of azomethines with Group II organometallic compounds, giving secondary amines on hydrolysis,[14] has not received much attention, and an even smaller number of intermediates have been isolated. The formation of the dimer $[EtMgN(Ph)CHEtPh]_2$, from diethylmagnesium and benzylideneaniline, suggests that the carbon–nitrogen double bond inserts into magnesium–carbon bonds.[15]

The small number of co-ordination complexes between ketones and beryllium alkyls is contrasted with the many isolated with azomethines as well as cyanides, some of which are coloured. Dimethylberyllium and PhCH=NMe initially give a yellow solution (ether, −78°) which fades as the solution warms, giving a colourless compound (II; R = Me, R′ = Me). Diphenylberyllium behaves similarly giving (II; R = Ph, R′ = Me). Replacement of the methyl group by a *p*-tolyl group in the latter complex gives the pale tan complex (II; R = Ph, R′ = *p*-MeC_6H_4). Though Me_2Be and $PhCH=NBu^t$ give a liquid, addition of pyridine yields Me_2Be,2py, in 61% yield. So, in absence of a complex disproportionation,

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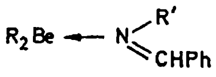
[13] G. E. Coates and S. I. E. Green, *J. Chem. Soc.*, 1962, 3340.
[14] M. Busch, *Chem. Ber.*, 1904, **37**, 2691.
[15] G. E. Coates and D. Ridley, *J. Chem. Soc.* (*A*), 1967, 56.

this azomethine also gives a co-ordination complex with Me_2Be.



(II)

As benzylideneaniline is used as an analytical reagent in the colourimetric estimation of organoaluminium compounds,[16] we were not surprised to find that Bu^t_2Be forms an orange-red complex (II; R = Bu^t, R′ = Ph) with PhCH=NPh. In contrast, the aliphatic azomethine Pr^iCH=NMe gives a colourless complex with Bu^t_2Be.

Alkyl cyanides also give colourless co-ordination complexes with beryllium alkyls. 2,2-Dimethylpropanonitrile gives monomeric complexes with both Bu^t_2Be and Bu^tBeCl. The former is recovered unchanged on heating at 60° for 9 h (contrast the low thermal stability of Bu^t_2Be and its ether complex).

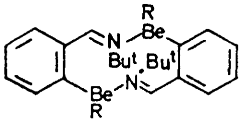
The preponderance of reduction products of ketones by beryllium alkyls which contain β-hydrogen atoms is not observed with azomethines. In only two instances have we observed products due to olefin elimination from the beryllium alkyl. Di-t-butylberyllium and PhCH=NMe form an orange solution at −78° in hexane which does not fade as the solution warms, though colourless $[Bu^tBeN(Me)CH_2Ph]_2$ crystallises, giving benzylmethylamine on hydrolysis. Di-t-butylberyllium and cinnamylideneaniline give $[Bu^tBeN(Ph)CH_2CH=CHPh]_2$ as colourless crystals from red-brown mother liquors. Since $PhCH=CHCH_2NHPh$ is isolated on hydrolysis, reduction occurred at the carbon atom *alpha* to the nitrogen atom rather than at the *gamma* carbon atom.

In no case did we observe diethylberyllium acting as a reducing agent towards azomethines, the isolated product being due to addition of one Be–C across C=N. Reaction of Et_2Be and PhCH=NMe gives colourless $[EtBeN(Me)CHEtMe]_2$ from a yellow solution. In a supplementary experiment, the volatile materials (collected in a vacuum system) were a mixture of ethylene and ethane corresponding to 94% addition. Diethylberyllium and benzylideneaniline similarly give $[EtBeN(Ph)CHEtPh]_2$. To measure the extent of addition, gas evolution was measured (vacuum line). The gas was a mixture of ethylene and ethane (20·4%). As the size of the organic group on the nitrogen atom increases so does the amount of gas evolution. The source of alkane elimination will be discussed below.

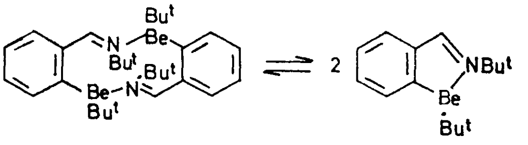
As expected, dimethylberyllium adds to the C=N bond. However, addition occurs only when the azomethine is an aniline derivative (see above). Addition of PhCH=NPh to Me_2Be results in a yellow solution (−78° and at ambient temperatures) from which colourless MeBeN(Ph)CHMePh crystallises, which is not sufficiently soluble in benzene to measure its molecular weight by methods currently available to us. The *p*-tolyl derivative [MeBeN(*p*-tolyl)CHMePh]$_2$ is sufficiently soluble in that solvent and is a dimer.

The dearth of reduction compounds and preponderance of addition compounds, a situation opposite to that found for aldehydes and ketones, is most easily explained by steric effects. The generally accepted mechanism for reduction of ketones by aluminium alkyls has the olefin elimination proceeding by formation of a cyclic six-membered transition state[17] and reduction by a four-membered transition state.[12] Since the six-membered ring requires more room than the four-membered ring, the group attached to nitrogen will determine the lowest energy pathway, assuming the ketone and azomethine reactions proceed by a similar mechanism. We then expect that as the group on nitrogen goes from methyl to phenyl the extent of reduction decreases, exactly as observed. Di-t-butylberyllium reduces PhCH=NMe, and forms a co-ordination complex with PhCH=NPh. In the former, olefin elimination occurs, since the methyl group does not force the t-butyl group, in the assumed six-membered ring transition state, too close to the methyl group. In the latter, reduction is prevented by the steric interference between the phenyl group on nitrogen and the t-butyl group on beryllium so olefin elimination cannot occur. Even with smaller groups on Be, olefin elimination is prevented. Thus Et_2Be adds to PhCH=NPh: the four-membered transition state is sterically accessible whereas the six-membered ring is not. The preceding assumes olefin elimination is thermodynamically favoured.

Much to our surprise, diethylberyllium appeared to reduce the highly sterically hindered $PhCH=NBu^t$, since the hydrolysable ethane to beryllium ratio of the yellow crystalline product was 1 : 1. However, measurement of the gas evolved during the reaction cleared up this anomaly. The only gas evolved was ethane (78·7%) over 46·5 h. Carbonylation of the product followed by hydrolysis gave *o*-formylbenzoic acid (phthaldehydic acid): a C=N i.r. stretching frequency at 1605 cm^{-1}, as well as the smell of benzaldehyde on hydrolysis, suggests the yellow dimer be formulated as the *ortho*-metallation product (III; R = Et) containing the cyclic $C_6Be_2N_2$ ten-membered ring system. Di-t-butylberyllium reacts analogously giving orange-yellow (III; R = Bu^t) whose degree of association, between 1·5 and 1·65 in benzene, suggests the equilibrium shown below. The colour of these unsymmetrical beryllium aryl–alkyls is likely due to charge transfer from the Be–C bond to the π*-orbitals of the aromatic ring. Thus, when the path



(III)



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[16] W. P. Neumann, *Annalen*, 1963, **667**, 12.

[17] E. C. Ashby and S. H. Yu, *J. Org. Chem.*, 1970, **35**, 1034.

for reduction or addition is blocked, abstraction of a hydrogen atom from the aromatic ring becomes the favoured reaction mechanism.

All of the alkylberyllium amides prepared in this study were crystallised from coloured solutions. Though the crystals are colourless, the development of colour suggests that metallation and complex formation proceed at rates competitive with those of reduction and addition. Further, alkane elimination found gasometrically in the reaction of Et_2Be with PhCH=NMe and PhCH=NPh is likely to be due to some metallation occurring simultaneously with addition.

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[18] under standard conditions. Alkoxy and aryl groups were in some instances determined by isolation and weighing of alcohol formed on hydrolysis. Other components were determined by established methods. ^1H N.m.r. spectra were recorded by use of a Varian HA-100 spectrometer in the solvent and internal reference specified. The i.r. absorptions, when reported, were recorded as Nujol mulls. Most 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.

Reaction of Benzophenone with Diphenylberyllium.—Benzophenone (0·29 g, 0·0016 mol) in benzene (5 ml) was added to diphenylberyllium[19] (0·26 g, 0·0016 mol) suspended in benzene (5 ml). The diphenylberyllium dissolved, and the yellow solution faded to colourless within minutes. After addition the solution was stirred for 30 min, benzene removed *in vacuo*, and the resulting white phenylberyllium triphenylmethoxide was crystallised as colourless *prisms* from toluene–hexane (1 : 1) in nearly quantitative yield. The compound shrank at *ca.* 90° and melted with decomposition at 162—165° when heated in a sealed capillary. The compound was not hydrolysed in 2N-H_2SO_4 nor 6N-HNO_3 as the solution did not contain any beryllium, however, a diethyl ether solution of it was readily hydrolysed by 2N-H_2SO_4 [Found: Be, 2·6; Ph_3CO, 74·4% (m.p. 162°, lit.,[20] 162°); *M* (cryoscopically, 1·53 and 1·15 w/w % in benzene), 718 and 720. $C_{50}H_{40}Be_2O_2$ requires Be, 2·6; Ph_3CO, 74·9%; *M*, 690].

With bis(trimethylsilylmethyl)beryllium. Addition of the ketone (0·55 g, 0·0031 mol) in benzene (5 ml) to $(Me_3SiCH_2)_2$-Be[21] (0·56 g, 0·0031 mol) in benzene (3 ml) gave a red colour which faded rapidly. After the mixture had been stirred for 15 min, the benzene was removed *in vacuo*, and the resulting solid $[Me_3SiCH_2BeOC(CH_2SiMe_3)Ph_2]_2$ yielded colourless *prisms* from hexane, m.p. 118—120° [Found: hydrolysable trimethylsilylmethyl, 24·2; Be, 2·6%; *M* (cryoscopically, 1·83 and 1·38 w/w %, in benzene), 650 and 656. $C_{42}H_{64}Be_2O_2Si_4$ requires hydrolysable trimethylsilylmethyl, 23·8; Be, 2·5%; *M*, 730].

With di-t-butylberyllium. The ketone (1·1 g, 0·0064 mol) in diethyl ether (20 ml) was added to di-t-butylberyllium–diethyl ether complex (1·3 g, 0·0064 mol) in diethyl ether (10 ml) at −78°. The violet colour which formed initially changed to a pale yellow at room temperature. The solution was stirred for 15 min, the solvent was removed in vacuum, and the yellow solid residue gave colourless *prisms* from hexane (−20°). When heated it softened at *ca.* 80°, became spongy at *ca.* 90°, and melted with decomposition at 101—103° [Found: hydrolysable butyl, 23·2; Be, 3·7%; *M* (cryoscopically, 0·85 and 0·58 w/w % in benzene), 507 and 495. $C_{34}H_{40}Be_2O_2$ requires hydrolysable butyl, 22·9; Be, 3·6%; *M*, 498]. Hydrolysis yielded benzhydrol which was identified by its m.p. 67—68° (lit.,[22] 67°). The alkoxide was recovered unchanged when refluxed in decalin for 3 h.

With diethylberyllium on a vacuum line. Diethylberyllium (0·105 g, 0·00157 mol) in hexane (2 ml) and the ketone (0·2860 g, 0·001570 mol) were mixed in a flask attached to a vacuum line. Ethylene (0·000664 mol) was the only gas collected, corresponding to 42·4% reduction. The resulting residue was not identified.

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Dimethylberyllium.*—Addition of the ketone (1·4 g, 0·010 mol) in diethyl ether (10 ml) to Me_2Be (0·34 g, 0·010 mol) in diethyl ether (15 ml) gave a colourless solution at −78°. After addition, with stirring, the diethyl ether was evaporated *in vacuo*, and the white residue of $(MeBeOCMeBu^t{}_2)_2$ crystallised from hexane as colourless *needles*, m.p. 89—91° [Found: hydrolysable methyl, 8·4; Be, 5·1%; *M* (cryoscopically, 1·19 and 0·89 w/w %, in benzene), 360 and 334. $C_{22}H_{48}Be_2O_2$ requires hydrolysable methyl, 8·3; Be, 5·0%; *M*, 362]. Hydrolysis gave 2,2,3,4,4-pentamethylpentan-3-ol identified by m.p. 40—41° (lit.,[23] 42·0—42·7°).

With diphenylberyllium. The ketone (0·75 g, 0·0053 mol) in diethyl ether (10 ml) and Ph_2Be (0·86 g, 0·0053 mol) in diethyl ether (20 ml) gave a colourless solution upon mixing. The solution was stirred for 15 min, the solvent removed, and the white residue of $Ph_2Be,OCBu^t{}_2$ crystallised from hexane–$Bu^t{}_2CO$ (20 : 1) as colourless *needles*, m.p. 75—76° [Found: hydrolysable phenyl, 50·6; $Bu^t{}_2CO$, 46·7; Be, 3·1%; *M* (cryoscopically, 1·00 and 0·75 w/w % in benzene), 307 and 317. $C_{21}H_{28}BeO$ requires hydrolysable phenyl, 50·6; $Bu^t{}_2CO$, 46·5; Be, 2·9%; *M*, 305]. The amount of benzene and $Bu^t{}_2CO$ were determined by weighing the combined volatile hydrolysis products which were shown to contain benzene and ketone in a 2 : 1 ratio by ^1H n.m.r. spectroscopy using CH_2Cl_2 as solvent and tetramethylsilane as internal reference. The i.r. spectrum contained absorptions at 1649s and 1567m cm^{-1}. After the complex had been boiled in toluene (12 h), it was recovered unchanged, as shown by m.p.

Diphenylberyllium–Bisquinuclidine.—Quinuclidine (0·29 g, 0·0027 mol) in diethyl ether (5 ml) was added to diphenylberyllium di-t-butyl ketone (0·43 g, 0·0014 mol) in diethyl ether (10 ml). After addition the suspension was stirred for 15 min, the solvent was removed, and the residue was crystallised as colourless star-like *needles* from benzene–hexane (2 : 1), m.p. 136—137° [Found: hydrolysable phenyl, 40·7; Be, 2·5%; *M* (cryoscopically, 0·75 and 0·57 w/w % in benzene), 257 and 259. $C_{26}H_{36}BeN_2$ requires hydrolysable phenyl, 40·0; Be, 2·3%; *M*, 385].

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In a separate experiment, the complex (0·68 g, 0·0017 mol) in benzene (5 ml) was evaporated (10^{-2} mmHg) to dryness. The recovered residue in the cold trap was shown to contain quinuclidine (0·00042 mol, 23·7 mol %) by titration using Methyl Red indicator.

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Bis*(*trimethylsilylmethyl*)*beryllium*.—Addition of the ketone (0·81 g, 0·0057 mol) in diethyl ether (10 ml) to $(Me_3SiCH_2)_2Be$ (1·0 g, 0·0057 mol) in diethyl ether gave no colour at −78°. After addition the solution was warmed to room temperature, stirred for 15 min, ether was evaporated *in vacuo*, and the resulting liquid could not be solidified. The i.r. spectrum contained an absorption at 1655s cm^{-1}, undoubtedly due to co-ordinated ketone as the uncomplexed ketone has an absorption at 1685s cm^{-1}.

In a separate experiment, $(Me_3SiCH_2)_2Be$ (0·920 g, 0·000504 mol) and Bu^t_2CO (0·0715 g, 0·000504 mol) were mixed for 30 min in a flask attached to the vacuum line. The resulting liquid liberated tetramethylsilane (0·00100 mol) on hydrolysis, indicating no significant addition to the carbonyl group had occurred.

With di-t-butylberyllium. The ketone (0·81 g, 0·0057 mol) in diethyl ether (10 ml) was added to di-t-butylberyllium–diethyl ether (1·1 g, 0·0057 mol) in diethyl ether (10 ml) at −78°. A yellow colour formed, and after warming to room temperature, stirring for 15 min, evaporation of ether *in vacuo* left a residue of $(Bu^tBeOCHBu^t_2)_2$ which crystallised from hexane as colourless *prisms*. When heated, it shrank at *ca*. 60° and melted at 84—86° [Found: hydrolysable butyl, 27·6; Be, 4·5%; *M* (cryoscopically, 1·95, 1·48, 0·70, and 0·52 w/w % in benzene), 413, 385, 360, and 335. $C_{26}H_{56}Be_2O_2$ requires hydrolysable butyl, 27·3; Be, 4·3%; *M*, 418]. Hydrolysis yielded 2,2,4,4-tetramethylpentan-3-ol identified by m.p. 50° (lit.,[24] 50°).

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Di-t-butylberyllium in a* 2 : 1 *Molar Ratio*.—The ketone (1·0 g, 0·0071 mol) in diethyl ether (10 ml) was added to di-t-butylberyllium–diethyl ether (1·4 g, 0·0071 mol) in diethyl ether at −78°. The yellow colour faded as the solution warmed to room temperature. Recooling to −78° did not regenerate colour. Another molar equivalent of ketone (1·0 g, 0·0071 mol) gave a yellow colour at −78° which faded to colourless as the solution warmed to room temperature. After stirring for 30 min, ether was removed, and the resulting residue of $(Bu^t_2CHO)_2Be$ was crystallised from benzene (50 ml) as colourless *needles*. When heated, it turned brown at *ca*. 390° without melting [Found: Be, 3·3; Bu^t_2CHO, 94·4% (m.p. of the alcohol, 50°, lit.,[24] 50°). $C_{18}H_{38}BeO_2$ requires Be, 3·1; Bu^t_2CHO, 96·9%]. The i.r. spectrum contained absorptions at 1395m, 1390m, 1376s, 1342w, 1243s,sh, 1232s,br, 1206s,br, 1059s, 1044m, 1030w, 1009s, 979m, 957w, 946w, 927w,sh, 921w, 876m, 854s, 770w, 721w, 673w, 645m, 531s, and 480s cm^{-1}. The alkoxide was independently prepared from diethylberyllium and the alcohol in a 1 : 2 molar ratio. 2,2,4,4-Tetramethylpentan-3-ol [25] (3·5 g, 0·024 mol) in diethyl ether (10 ml) was added to the diethyl ether complex of diethylberyllium (1·7 g, 0·012 mol) in diethyl ether at −78°. After addition and warming to room temperature, the solution was stirred for 30 min. The volatile material was removed *in vacuo* and the resulting residue crystallised from toluene (70 ml) as colourless needles, shown to be $(Bu^t_2CHO)_2Be$ by its i.r. spectrum.

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Di-t-butylberyllium and* NNN′N′-*Tetramethylethylenediamine*.—The ketone (0·93 g, 0·0066 mol) in hexane (3 ml) was added to Bu^t_2Be,tmed [26] (1·6 g, 0·0066 mol) in hexane at −78°. A yellow colour formed and after the solution was warmed to room temperature and the colourless solution stirred for 15 min, the hexane was removed *in vacuo*, resulting in a white residue which crystallised from hexane as colourless *prisms*, shown to be $(Bu^tBeOCHBu^t_2)_2$ by m.p. 84—87°.

In a separate experiment Bu^t_2CO was added to Bu^t_2Be,-OEt_2 at −78° in diethyl ether, immediately followed by tmed. The yellow colour intensity did not perceptibly change. On warming to room temperature the yellow colour faded to colourless. The solvent was removed *in vacuo*, resulting in a white solid which crystallised as colourless *prisms*, shown to be $(Bu^tBeOCHBu^t_2)_2$ by m.p. 83—86°.

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Di-t-butylberyllium and Quinuclidine*.—The ketone (1·2 g, 0·0084 mol) in diethyl ether (5 ml) was added to Bu^t_2Be,-OEt_2 (1·6 g, 0·0084 mol) in diethyl ether (5 ml) at −78°. To the yellow solution (−78°) quinuclidine (0·92 g, 0·0084 mol) in diethyl ether (5 ml) was added with no perceptible colour change. After addition, the colour changed to colourless as the solution warmed to room temperature. After stirring for 15 min, ether was evaporated, and the resulting residue of $(Bu^tBeOCHBu^t_2,NC_7H_{13})$ crystallised as colourless needles from hexane (−10°), m.p. 67—69° [Found: hydrolysable butyl, 18·0; Be, 3·0%; *M* (cryoscopically, 1·44 and 1·09 w/w % in benzene), 306 and 303. $C_{20}H_{41}BeNO$ requires hydrolysable butyl, 17·8; Be 2·9%; *M*, 320]. Hydrolysis yielded 2,2,4,4-tetramethylpentan-3-ol identified by m.p. 50° (lit.,[24] 50°).

In another experiment, the ketone was added to di-t-butylberyllium–quinuclidine (see below) in diethyl ether at −78°. A yellow-orange colour appeared which faded as the solution warmed to room temperature. After stirring for 30 min, and after removal *in vacuo* of ether the white solid crystallised from hexane (−10°) and was shown to be the quinuclidine complex of $Bu^tBeOCHBu^t_2$ by m.p. 66—68°.

Di-t-Butylberyllium–Quinuclidine.—Quinuclidine (0·93 g, 0·0084 mol) in hexane (5 ml) was added to di-t-butylberyllium–diethyl ether (1·6 g, 0·0084 mol) in hexane (5 ml). After addition and after stirring for 15 min, the hexane was evaporated, and the *adduct* was crystallised from hexane. When heated, it shrank at *ca*. 60° and melted at 78—79° [Found: hydrolysable butyl, 49·4; Be, 3·9%, *M* (cryoscopically, 1·26 and 0·95 w/w % in benzene) 231 and 226. $C_{15}H_{31}BeN$ requires hydrolysable butyl, 48·8; Be, 3·8%; *M*, 234].

t-Butylberyllium 2,2,4,4-*Tetramethylpentan*-3-*oxide*-4-NN-*Dimethylaminopyridine*.—4-*NN*-Dimethylpyridine (0·45 g, 0·0037 mol) in toluene (5 ml) was added to $(Bu^tBeOCHBu^t_2)_2$ (0·79 g, 0·0038 mol) in toluene (10 ml). The mixture was stirred for 15 min, the toluene was evaporated and the white residue crystallised from hexane as colourless *plates*, m.p. 110—111° [Found: hydrolysable butyl, 17·8; Be, 2·9%; *M* (cryoscopically, 1·34 and 1·01 w/w % in benzene), 338 and 333. $C_{20}H_{38}BeN_2O$ requires hydrolysable butyl, 17·2; Be, 2·7%; *M*, 331.

Reaction of 2,2,4,4-*Tetramethylpentan*-3-*one with Di-isobutylberyllium*.—The ketone (3·3 g, 0·023 mol) in hexane (10 ml) was added to di-i-butylberyllium diethyl ether complex (4·35 g, 0·023 mol) in hexane (20 ml) at −78°. The yellow colour which formed slowly faded as the solution

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warmed to room temperature. The solution was stirred for 30 min, hexane was removed, and the white residue of $(Bu^{i}BeOCHBu^{t}_{2})_{2}$ crystallised from hexane–benzene (2 : 1) as colourless *plates*, m.p. 171—172° [Found: hydrolysable butyl, 28·0; Be, 4·5%; *M* (cryoscopically, 1·47 and 1·07 w/w % in benzene), 416 and 396. $C_{26}H_{56}Be_{2}O_{2}$ requires hydrolysable butyl, 27·3; Be, 4·3%; *M*, 418]. The alkoxide did not react with further ketone, $(Bu^{i}BeOCHBu^{t}_{2})_{2}$ was recovered after mixture with a five-fold excess of $Bu^{t}_{2}CO$.

With diethylberyllium. The ketone (3·1 g, 0·022 mol) in hexane (10 ml) was added to diethylberyllium–diethyl ether (1·9 g, 0·022 mol) in hexane at −78°. A yellow colour formed which faded to colourless as the solution warmed to room temperature. The solution was stirred for 15 min, the ether was removed, and the resulting white residue of $(EtBeOCHBu^{t}_{2})_{2}$ crystallised from hexane as colourless *plates*, m.p. 147—148° [Found: hydrolysable ethyl, 16·9; Be, 4·8%; *M* (cryoscopically, 1·60 and 1·20 w/w % in benzene), 364 and 378. $C_{22}H_{48}Be_{2}O_{2}$ requires hydrolysable ethyl, 16·0; Be, 5·0%; *M*, 362]. Hydrolysis gave 2,2,4,4-tetramethylpentan-3-ol identified by m.p. 50° (lit.,[24] 50°). When the alkoxide with additional ketone was boiled with reflux in xylene for 3 h, only unreacted $(EtBeOCHBu^{t}_{2})_{2}$ was recovered.

In a separate experiment, $Bu^{t}_{2}CO$ (0·001960 g, 0·001380 mol) and $Et_{2}Be$ (0·000925 g, 0·00138 mol) in hexane (2 ml) were mixed in a flask attached to the vacuum line. The only gas evolved was ethylene (0·00138 mol) indicating quantitative reduction.

With t-butylberyllium chloride. The ketone (1·9 g, 0·013 mol) in diethyl ether (5 ml) was added to $Bu^{t}BeCl$ prepared from beryllium chloride–bis(diethyl ether) (1·5 g, 0·0066 mol) and di-t-butylberyllium–diethyl ether (1·3 g, 0·0066 mol) in diethyl ether (30 ml) at −78°. The yellow solution was warmed to room temperature and the now colourless solution was stirred for 15 min. The ether was evaporated and the residue of $(ClBeOCHBu^{t}_{2})_{2}$ crystallised from benzene as colourless *prisms*. When heated, it became brown at *ca.* 190° and did not melt [Found: Be, 5·0; Cl, 18·0%; *M* (cryoscopically, 0·61 and 0·45 w/w % in benzene), 346 and 352. $C_{18}H_{38}Be_{2}Cl_{2}O_{2}$ requires Be, 4·8; Cl, 19·0%; *M*, 355]. Hydrolysis yielded 2,2,4,4-tetramethylpentan-3-ol identified by m.p. 49° (lit.,[24] 50°). The i.r. spectrum consisted of absorptions at 1400m, 1378s, 1247w, 1212w, 1165w, 1135w, 1048s, 1040m, 1008s, 949s, 935s, 882m, 839m, 760w, 522w, and 461m cm^{-1}.

With cyclopentadienyl(t-butyl)beryllium. The ketone (0·57 g, 0·0041 mol) in hexane (5 ml) was added to $(C_{5}H_{5})BeBu^{t}$ [27] (0·53 g, 0·0041 mol) in hexane (5 ml) at −78° without observable colour change. The solution was warmed to room temperature and stirred for 30 min. Hexane was removed and the residue was shown to be $(C_{5}H_{5})BeBu^{t}$ by m.p., 40°.

Reaction of 2,2-Dimethylpropanal with Di-t-Butylberyllium.—The aldehyde (0·76 g, 0·0088 mol) in diethyl ether (10 ml) was added to di-t-butylberyllium–diethyl ether (1·7 g, 0·0088 mol) in diethyl ether (10 ml) by way of an orange-red colour at −78°. After addition, the solution was warmed to room temperature and the colourless solution was stirred for 15 min. Ether was evaporated and the residue of $(Bu^{t}BeOCH_{2}Bu^{t})_{2}$ was crystallised from hexane (−10°) as colourless needles, m.p. 213—215° [Found: hydrolysable butyl, 36·9; Be, 6·2%; *M* (cryoscopically, 0·91 and 0·68 w/w % in benzene), 327 and 329. $C_{18}H_{40}Be_{2}O_{2}$ requires hydrolysable butyl, 37·2; Be, 5·9%; *M*, 306].

With di-isobutylberyllium. The aldehyde (1·6 g, 0·0018 mol) in hexane (15 ml) was added to di-isobutylberyllium–diethyl ether (3·4 g, 0·018 mol) in hexane (20 ml) at −78°. The red-orange colour faded to colourless as the solution warmed to room temperature. The solution was stirred at room temperature for 15 min, hexane was removed, and the liquid was distilled at 80—85°/10^{-3} mmHg (bath temperature 120—130°) [Found: hydrolysable butyl, 37·9; Be, 5·6%; *M* (cryoscopically, 1·04 and 0·77 w/w % in benzene), 434 and 428. $C_{27}H_{60}Be_{3}O_{3}$ requires hydrolysable butyl, 37·1; Be, 5·9%; *M*, 459]. The i.r. spectrum contained absorptions at 1478m, 1462m, 1400w, 1382w, 1360m, 1310m, 1185m, 1078s, 1018m, 978m, 925w, 900w, 880w, 830w, 805w, 785w, and 635w cm^{-1}. The product, $(Bu^{i}BeOCH_{2}Bu^{t})_{3}$, reacts with additional aldehyde giving benzene insoluble $(Bu^{t}CH_{2}O)_{2}Be$. When heated, it did not melt to 300° [Found: Be, 5·0%. $C_{10}H_{22}BeO_{2}$ requires Be, 4·9%]. Hydrolysis gives 2,2-dimethylpropanol identified by m.p. 51° (lit.,[28] 52—53°).

With diethylberyllium. The aldehyde (0·1412 g, 0·001640 mol) and diethylberyllium (0·110 g, 0·00164 mol) in hexane (2 ml) were mixed in a flask attached to the vacuum line. Ethylene (0·00128 mol) was the only gas evolved, corresponding to 78·4% reduction. The residue was not characterised.

With t-butylberyllium chloride. The aldehyde (1·1 g, 0·0013 mol) in diethyl ether (5 ml) was added to t-butylberyllium chloride prepared from beryllium chloride–bis(diethyl ether) (1·6 g, 0·00068 mol) and di-t-butylberyllium–diethyl ether (1·3 g, 0·00068 mol) in diethyl ether (25 ml) at −78°. The orange-red coloured mixture yielded a colourless suspension at room temperature. The suspension was stirred for 15 min, ether was removed, and the residue gave large, colourless, *prisms* of $(ClBeOCH_{2}Bu^{t},OEt_{2})_{1-2}$ from benzene–ether (5 : 1). When heated, it shrank at *ca.* 110° and melted at 162° [Found: Be, 4·6; Cl, 17·0%; *M* (cryoscopically, 2·16, 1·38, and 1·08 w/w % in benzene), 348, 336, and 295. $C_{18}H_{42}Be_{2}Cl_{2}O_{4}$ requires Be, 4·4; Cl, 17·3%; *M*, 411].

The diethyl ether complex (0·0005 mol) was put into a flask attached to the vacuum line and heated at 100° for 24 h and 135° for 12 h to remove ether quantitatively. When heated, the benzene-insoluble $ClBeOCH_{2}Bu^{t}$ turned brown at *ca.* 250° and did not melt [Found: Be, 6·5; Cl, 25·9%. $C_{5}H_{11}BeClO$ requires Be, 6·8; Cl, 27·0%]. The i.r. spectrum contained absorptions at 1315w, 1255w, 1037s, 1015s, 925m, 897w, 870m, 802s, 747m, 705m, and 529m cm^{-1}.

Bis(chloroberyllium-2,2-dimethylpropoxide)-NNN′N′-tetramethylethylenediamine, $(ClBeOCH_{2}Bu^{t})_{2}$,tmed.—Excess of diamine was added to $ClBeOCH_{2}Bu^{t},OEt_{2}$ (0·85 g, 0·0052 mol) dissolved in benzene (10 ml). The resulting white suspension was stirred for 15 min, benzene removed *in vacuo*, and the residue crystallised from benzene (25 ml). When heated it shrank at *ca.* 200°, and did not melt [Found: Be, 5·0; Cl, 18·5%. $C_{16}H_{38}Be_{2}Cl_{2}N_{2}O_{2}$ requires Be, 4·8; Cl, 18·7%]. The i.r. spectrum contained absorptions at 1452w, 1365m, 1356m, 1316w, 1301w, 1259w, 1230w, 1206w, 1175w, 1180m,sh, 1071s, 1045m,sh, 1040s, 1018s, 954s, 933s, 920w, 897w, 806s, 790m, 755s, 710s, 681s, and 617m cm^{-1}.

t-Butylberyllium Isopropoxide, $(Bu^{t}BeOPr^{i})_{2}$.—Acetone (0·38 g, 0·0066 mol) in diethyl ether (10 ml) was added to di-t-butylberyllium–diethyl ether (1·3 g, 0·0066 mol) in diethyl ether (10 ml) at −78°. A yellow colour formed,

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[27] G. E. Coates, D. L. Smith, and R. C. Srivastava, *J.C.S. Dalton*, 1973, 618.

[28] L. E. Tissier, *Angew. Chem.*, 1916, **29**, 340.

which completely disappeared on warming to room temperature and stirring for 1 h. The volatile materials were removed and the pale yellow residue gave colourless *prisms* from hexane (0°), m.p. 95° [Found: hydrolysable butyl, 46·0; Be, 7·4%; *M* (cryoscopically, 1·01 and 0·76 w/w % in benzene), 263 and 265. $C_{14}H_{32}Be_2O_2$ requires hydrolysable butyl, 45·6; Be, 7·2%; *M*, 250]. In a separate experiment, acetone and Bu^t_2Be,OEt_2 were mixed in a flask attached to the vacuum line; but-1-ene and diethyl ether were the only two gases evolved, as shown by the i.r. spectrum.

t-Butylberyllium Triphenylmethoxide, $(Bu^tBeOCPh_3)_2$.—Triphenylmethanol (1·4 g, 0·0053 mol) in diethyl ether (15 ml) was added to di-t-butylberyllium–diethyl ether (1·0 g, 0·0053 mol) dissolved in diethyl ether (10 ml) at −78°. After addition, the pale pink solution was warmed to room temperature, stirred for 15 min, and the ether removed giving a white spongy residue which crystallised from benzene as colourless *prisms*. When heated, it softened at *ca.* 120° and melted at 141—143° [Found: hydrolysable butyl, 17·8; Be, 2·8%; *M* (cryoscopically, 0·85 and 0·60 w/w % in benzene), 646 and 635. $C_{46}H_{48}Be_2O_2$ requires hydrolysable butyl, 17·6; Be, 2·8%; *M*, 650].

Beryllium Bis(2,2,4,4-*tetramethyl*-3-*ethylpentyl oxide*), $(Bu^t_2EtCO)_2Be$.—This was prepared by addition of 2,2,4,4-tetramethyl-3-ethylpentanol[29] (3·9 g, 0·023 mol) in diethyl ether (15 ml) to diethylberyllium–diethyl ether (1·3 g, 0·011 mol) in diethyl ether (10 ml) at −78°. After the addition, the solution was warmed to room temperature, stirred for 15 min, and the solvent was evaporated leaving a white residue which gave colourless *needles* from benzene (40 ml), m.p. 205—207° (decomp.) [Found: Be, 2·6; Bu^t_2EtCO, 96·5%. $C_{22}H_{46}BeO_2$ requires Be, 2·6; Bu^t_2EtCO, 97·4%].

Non-reaction of Di-t-butoxyberyllium with Quinuclidine.—The amine (1·1 g, 0·0099 mol) in hexane (5 ml) was stirred with $Be(OBu^t)_2$ (0·77 g, 0·0050 mol) in hexane (5 ml) for 1 h. The hexane was removed in vacuum and the residue was crystallised as colourless *plates* from hexane (−30°), m.p. 112°. The m.p. of $Be(OBu^t)_2$ is 112°.[11]

Reaction of N-*Benzylideneaniline with Di-t-butylberyllium*.—*N*-Benzylideneaniline[30] (1·1 g, 0·0061 mol) in diethyl ether (10 ml) was added to di-t-butylberyllium–diethyl ether (1·2 g, 0·0061 mol) in diethyl ether (10 ml) at −78°. The red solution was warmed to room temperature, stirred for 30 min, the ether evaporated, and the red residue crystallised as orange-red *prisms* of $[Bu^t_2BeN(Ph)CHPh]$ from hexane, m.p. 128—130° [Found: hydrolysable butyl, 37·0; Be, 2·8%; *M* (cryoscopically, 0·82 and 0·56 w/w % in benzene), 300 and 278. $C_{21}H_{29}BeN$ requires hydrolysable butyl, 37·6; Be, 3·0%; *M*, 304]. The i.r. spectrum contained absorptions in the 1600—1500 cm^{-1} region at 1605m, 1595w, and 1581m cm^{-1}.

With diethylberyllium. The azomethine (1·9 g, 0·011 mol) in diethyl ether (10 ml) was added to diethylberyllium–diethyl ether (1·1 g, 0·011 mol) in diethyl ether at −78°. After addition, the yellow solution was warmed to room temperature, stirred for 30 min, ether was removed *in vacuo*, and the resulting yellow residue was crystallised from hexane–benzene (6 : 1) as colourless *prisms* of $[EtBeN(Ph)CHEtPh]_2$ (yield, 0·7 g, 28%). When heated, it softened at *ca.* 90° and melted at 134—136° [Found: hydrolysable ethyl, 11·7; Be, 3·7%; *M* (cryoscopically, 1·47 and 1·11 w/w % in benzene), 456 and 464. $C_{34}H_{42}Be_2N_2$ requires hydrolysable ethyl, 11·7; Be, 3·6%; *M*, 496]. Hydrolysis of the dimer with dilute nitric acid yielded *N*-phenyl-*N*-(1-phenylpropyl)amine nitrate which had m.p. 173—174° (decomp.) (lit.,[31] 174°).

In another experiment, diethylberyllium (0·135 g, 0·00202 mol) and the azomethine (0·3879 g, 0·002142 mol) were mixed in a flask attached to the vacuum line. During 31 h at room temperature ethylene and ethane (0·000411 mol) were collected, corresponding to 79·6% addition.

With dimethylberyllium. The azomethine (1·8 g, 0·010 mol) in diethyl ether (5 ml) was added to Me_2Be (0·39 g, 0·010 mol) in diethyl ether (5 ml) at −78°. Most of the product had precipitated when the addition was complete. The yellow suspension was warmed to room temperature, stirred for 2 h, ether removed *in vacuo*, and the yellow residue of [MeBeN(Ph)CHMePh] crystallised from toluene (10 ml) as colourless *needles*. The product shrank at *ca.* 140° and melted at 153—154° [Found: hydrolysable methyl, 6·8; Be, 4·2%. $C_{15}H_{17}BeN$ requires hydrolysable methyl, 6·8; Be, 4·1%]. Hydrolysis with dilute sulphuric acid yielded *N*-phenyl-*N*-(1-phenylethyl)amine sulphate identified by m.p. 140—141° (lit.,[32] 142—143°).

Reaction of N-*Benzylidene-*p*-toluidine with Dimethylberyllium*.—*N*-Benzylidene-*p*-toluidine[33] (1·1 g, 0·0056 mol) in diethyl ether (5 ml) was added to dimethylberyllium (0·22 g, 0·0055 mol) in diethyl ether at −78°. The pale yellow solution was warmed to room temperature, stirred for 1 h, diethyl ether evaporated, and the pale yellow residue of $[MeBeN(p\text{-}MeC_6H_4)CHMePh]_2$ crystallised as colourless *prisms* from hexane (brown mother liquors) in 28% (0·36 g) yield, m.p. 155—156° (decomp.) [Found: hydrolysable methyl, 6·4; Be, 3·7%; *M* (cryoscopically, 1·11 and 0·84 w/w % in benzene), 453 and 468. $C_{32}H_{38}Be_2N_2$ requires hydrolysable methyl, 6·4; Be, 3·8%; *M*, 468]. *N*-*p*-Tolyl-*N*-(1-phenylethyl)amine was identified by m.p. 85—87° of its *p*-toluenesulphonyl derivative (lit.,[34] 86—87°).

With diphenylberyllium. The azomethine (0·36 g, 0·0018 mol) in diethyl ether (5 ml) was added to Ph_2Be (0·30 g, 0·0018 mol) in diethyl ether (5 ml). After addition the colourless solution was stirred for 1 h, diethyl ether was evaporated, and the pale red solid gave tan *prisms* of $[Ph_2BeN(p\text{-}MeC_6H_4)CHPh]_2$ (0·40 g, 61%) from hexane–benzene (1 : 1). The complex shrank at *ca.* 100° and melted at 134—135° [Found: hydrolysable phenyl, 42·7; Be, 2·7%; *M* (cryoscopically, 1·18 and 0·89 w/w % in benzene), 368 and 361. $C_{26}H_{23}BeN$ requires hydrolysable phenyl, 43·1; Be, 2·5%; *M*, 358]. The i.r. spectrum in the 1650—1550 cm^{-1} region contained absorptions at 1615m, 1590m, and 1575w cm^{-1}.

Reaction of N-*Benzylidenemethylamine with Di-t-butylberyllium*.—*N*-Benzylidenemethylamine[35] (0·67 g, 0·0055 mol) in hexane (5 ml) was added to di-t-butylberyllium diethyl ether complex (1·1 g, 0·0055 mol) in hexane (5 ml) at −78°. The solution was dark brown but became orange as it warmed to room temperature. The orange solution was stirred for 2 h, hexane was evaporated, and the orange viscous liquid solidified on pumping *in vacuo* (10^{-2} mmHg) for 3 h, followed by addition of hexane (2 ml). Colourless *prisms* of $[Bu^tBeN(Me)CH_2Ph]_2$ were obtained from hexane, and sublimed at 120—130°, 10^{-2} mmHg. The product

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shrank at *ca.* 170° and melted at 325—327° (decomp.) [Found: hydrolysable butyl, 30·8; Be, 4·9%; *M* (cryoscopically, 1·46 and 1·10 w/w % in benzene), 377 and 380. $C_{24}H_{38}Be_2N_2$ requires hydrolysable butyl, 30·7; Be, 4·8; *M*, 372]. *N*-Benzyl-*N*-methylamine, formed on hydrolysis, was identified by its picrate, m.p. 116—117° (lit.,[36] 117—118°). In a separate experiment, $[Bu^tBeN(Me)CH_2Ph]_2$ was recovered unchanged on admixture with the azomethine.

With diethylberyllium. Addition of the azomethine (1·6 g, 0·013 mol) in hexane (5 ml) to diethylberyllium–diethyl ether (1·2 g, 0·013 mol) in hexane (5 ml) resulted in a yellow solution. The mixture was stirred for 2 h, when evaporation of hexane left a yellow liquid which solidified on pumping *in vacuo* (10^{-2} mmHg) overnight. The solid crystallised (1·5 g, 73%) as colourless *needles* of $[EtBeN(Me)CHEtPh]_2$ from hexane (5°), though the mother liquor was yellow, m.p. 82—84° [Found: hydrolysable ethyl, 15·5; Be, 4·8%; *M* (cryoscopically, 1·61 and 1·21 w/w % in benzene), 360 and 356. $C_{24}H_{38}Be_2N_2$ requires hydrolysable ethyl, 15·6; Be, 4·8%; *M*, 372]. In a separate experiment, Et_2Be (0·125 g, 0·00187 mol) and PhCH=NMe (0·2396 g, 0·002014 mol) were mixed in a flask attached to a vacuum line. Ethane and ethylene (0·000104 mol), corresponding to 94·4% addition, were collected at room temperature during 48 h.

With dimethylberyllium. The azomethine (0·60 g, 0·0050 mol) in diethyl ether (5 ml) was added to Me_2Be (0·19 g, 0·0050 mol) in diethyl ether (5 ml) at −78°. A pale yellow colour formed which faded to colourless within seconds. After addition, the solution was stirred for 2 h, and evaporation of diethyl ether yielded a white solid complex, $Me_2Be,N(Me)=CHPh$, which had m.p. 60—62° after sublimation at 45—50°, 10^{-2} mmHg [Found: hydrolysable methyl, 18·7; Be, 5·6%; *M* (cryoscopically, 1·24 and 0·93 w/w % in benzene), 179 and 182. $C_{10}H_{15}BeN$ requires hydrolysable methyl, 19·0; Be, 5·7%; *M*, 158]. The i.r. spectrum contained an absorption at 1490m cm^{-1} in the 1650—1450 cm^{-1} region.

With diphenylberyllium. The azomethine (0·20 g, 0·0017 mol) and Ph_2Be (0·28 g, 0·0017 mol) were stirred in diethyl ether (10 ml) for 1 h. The volatile materials were removed *in vacuo* and the white solid gave colourless *needles* of $Ph_2Be,N(Me)=CHPh$ from benzene–hexane (1 : 1) in 63% (0·30 g) yield, m.p. 122—124° [Found: hydrolysable phenyl, 55·3; Be, 3·2%; *M* (cryoscopically, 1·06 and 0·80 w/w % in benzene), 278 and 284. $C_{20}H_{19}BeN$ requires hydrolysable phenyl, 54·6; Be, 3·2%; *M*, 282]. The i.r. spectrum contained, in the 1650—1550 cm^{-1} region, absorptions at 1630s and 1590s cm^{-1}.

*t-Butyl-2-(*N*-t-butylformimidoylphenyl)beryllium* (III; R = Bu^t).—*N*-Benzylidene-t-butylamine[37] (1·6 g, 0·0097 mol) in hexane (5 ml) was added to di-t-butylberyllium–diethyl ether (1·9 g, 0·0097 mol) in hexane (15 ml). A red colour formed and did not disappear on stirring for 12 h. The hexane was removed *in vacuo*, the brown liquid solidified on addition of hexane (5 ml), and was crystallised as orange-red *needles* from hexane–benzene (3 : 1) in 27% (0·6 g) yield. The product sublimed at 70—75°, 10^{-2} mmHg, shrank at *ca.* 120°, and melted at 128—129°. The yield was increased to 50% by stirring for 47 h rather than 12 h [Found: hydrolysable butyl, 25·4; Be, 4·1%; *M* (cryoscopically, 2·01, 1·41, and 1·06 w/w % in benzene), 373, 355, and 338. $C_{30}H_{46}Be_2N_2$ requires hydrolysable butyl, 25·2; Be, 4·0%; *M*, 452]. The i.r. spectrum in the 1600—1450 cm^{-1} region contained absorptions at 1600s and 1530w cm^{-1}.

The compound was dissolved in diethyl ether, an excess of solid carbon dioxide was added, and solution was stirred for 24 h. The solution was hydrolysed with 2N-H_2SO_4, extracted with diethyl ether (3 × 10 ml), ether was evaporated, and the brown oil shown to be phthaldehydic acid by m.p. 203—205° (decomp.) of its semicarbazone derivative (lit.,[38] 202°).

*Ethyl-2-(*N*-t-butylformimidoylphenyl)beryllium* (III; R = Et).—*N*-Benzylidene-t-butylamine (1·4 g, 0·0089 mol) in hexane (5 ml) was added to diethylberyllium–diethyl ether (0·80 g, 0·0089 mol) in hexane (5 ml) at −78°. The orange-yellow solution was warmed to room temperature, stirred for 4 h, hexane removed *in vacuo*, the resulting orange liquid pumped *in vacuo* (10^{-2} mmHg) overnight, and the resulting residue crystallised as yellow prisms from benzene–hexane (1 : 2) (yield 0·88 g, 50%). The compound shrank at 120° and melted at 122—124° [Found: hydrolysable ethyl, 14·5; Be, 4·8%; *M* (cryoscopically, 1·56 and 1·18 w/w % in benzene), 383 and 383. $C_{26}H_{38}Be_2N_2$ requires hydrolysable ethyl, 14·7; Be, 4·6%; *M*, 396]. The i.r. spectrum contained absorptions at 1605s and 1540m cm^{-1} in the 1600—1450 cm^{-1} region.

The metallated product was dissolved in diethyl ether (30 ml) and an excess of solid carbon dioxide was cautiously added. The solution was stirred for 12 h, then hydrolysed with 2N-H_2SO_4, extracted with diethyl ether (3 × 20 ml), dried ($MgSO_4$), ether was evaporated, and the brown oil was shown to be phthaldehydic acid by m.p. 203—204° (decomp.) of its semicarbazone derivative (lit.,[38] 202°).

In a separate experiment, the azomethine (1·48 g, 0·00923 mol) and Et_2Be (0·608 g, 0·00908 mol) were mixed in a flask attached to the vacuum line. The only gas collected in 46·5 h was ethane (0·00714 mol), indicating 78·7% metallation.

Reaction of N*-Benzylidene-t-butylamine and Dimethylberyllium.*—The azomethine (0·81 g, 0·0050 mol) in hexane (5 ml) was added to Me_2Be (0·19 g, 0·0050 mol) in diethyl ether (5 ml). The yellow solution was stirred for 1 h, solvents were removed *in vacuo*, resulting in a yellow liquid which would not solidify. Pyridine (0·79 g, 0·0010 mol) was added to the complex in hexane (5 ml), the resulting solid crystallised from hexane–benzene (2 : 1) in 61% (0·60 g) yield and shown to be $Me_2Be,2py$ by m.p. 87—89° (lit.,[13] 91—92°).

*Di-t-butylberyllium–*N*(2,2-dimethylethylidene)methylamine*, $Bu^t{}_2Be,N(Me)=CHPr^i$.— *N*-Isopropylidenemethylamine[39] (0·68 g, 0·0080 mol) in hexane (2 ml) was added to di-t-butylberyllium–diethyl ether (1·6 g, 0·0080 mol) in hexane (5 ml) at −78°. The pale yellow suspension dissolved as it warmed to room temperature. The solution was stirred for 1 h, hexane was removed, and the white solid residue was crystallised as colourless *plates* from hexane (−5°), m.p. 34° [Found: hydrolysable butyl, 54·4; Be, 4·5%; *M* (cryoscopically, 1·22 and 0·92 w/w % in benzene), 211 and 209. $C_{13}H_{29}BeN$ requires hydrolysable butyl, 54·8; Be, 4·3%; *M*, 208]. The i.r. spectrum in the 1700—1500 cm^{-1} region contained an absorption at 1670s cm^{-1}.

t-Butylberyllium N*-(3-Phenylprop-2-enyl)phenylamide*, $[Bu^tBeN(Ph)CH_2CH=CHPh]_2$.— *N*-(3-phenylprop-3-enylidene)aniline[40] (2·0 g, 0·0098 mol) in diethyl ether (15 ml)

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was added to di-t-butylberyllium–diethyl ether (1·9 g, 0·0089 mol) in diethyl ether (10 ml) at −78°. After addition, the red solution warmed to room temperature and was stirred for 1 h, diethyl ether was removed *in vacuo*, and the red-brown residue crystallised as colourless *prisms* from hexane. The product shrank at *ca.* 100° and melted at 130—133° (decomp.) [Found: hydrolysable butyl, 20·3; Be, 3·2%; *M* (cryoscopically, 1·75 and 1·32 w/w % in benzene), 575 and 560. $C_{38}H_{46}Be_2N_2$ requires hydrolysable butyl, 20·7; Be, 3·3%; *M*, 550]. Hydrolysis yielded *N*-(3-phenylprop-2-enyl)aniline identified by m.p. 134—136° (decomp.) of its picrate derivative (lit.,[41] m.p. 137°).

Di-t-butylberyllium–t-Butyl Cyanide, $Bu^t_2Be,NCBu^t$.—t-Butyl cyanide (0·49 g, 0·0060 mol) in hexane (5 ml) was added to di-t-butylberyllium–diethyl ether (1·1 g, 0·0060 mol) in hexane (5 ml) at −78°. After addition, the pale yellow solution was warmed to room temperature, stirred for 30 min, hexane was removed, and the white residue crystallised as colourless *needles* from hexane (0°), m.p. 27—28° [Found: hydrolysable butyl, 56·8; Be, 4·3%; *M* (cryoscopically, 0·55 and 0·41 w/w % in benzene), 237 and 226. $C_{13}H_{27}BeN$ requires hydrolysable butyl, 55·4; Be, 4·4%; *M*, 206]. The i.r. spectrum contained an absorption at 2290s cm^{-1}. The complex was recovered after heating in hexane for 8 h at 50° followed by further heating at 65° for 9 h.

t-Butylberyllium Chloride–t-Butyl Cyanide, $Bu^tBeCl,NCBu^t$.—The nitrile (0·90 g, 0·011 mol) in diethyl ether (2 ml) was added to t-butylberyllium chloride, prepared from beryllium chloride–bis(diethyl ether) (1·2 g, 0·0054 mol) and di-t-butylberyllium–diethyl ether (1·1 g, 0·0054 mol) in diethyl ether (20 ml). The complex precipitated during addition. After addition, the suspension was stirred for 15 min, diethyl ether was removed, and the residue crystallised as colourless *prisms* from benzene–hexane (2 : 1). When heated it shrank at *ca.* 50°, softened at *ca.* 70°, turned brown at *ca.* 150°, and became white at *ca.* 180° [Found: Be, 4·9; Cl, 20·0%; *M* (cryoscopically, 1·0 and 0·74 w/w % in benzene), 185 and 163. $C_9H_{18}BeClN$ requires Be, 4·9; Cl, 19·3%; *M*, 184·5]. The i.r. spectrum contained an absorption at 2300s cm^{-1}.

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