Alkoxyberyllium Tetrahydroborates: t-Butoxyberyllium Pentane-2,4-dionate and Complexes of t-Butoxyberyllium Oxide

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The tetrahydroborates $Me_2EtCOBeBH_4$ and $Et_3COBeBH_4$ are dimeric in contrast to monomeric $(BH_4)_2Be_3(OBu^t)_4$. t-Butoxyberyllium tetrahydroborate is unreactive to olefins and does not reduce acetone or benzophenone in toluene, but reduces benzophenone in ether. With acetone and tetrahydrofuran, the oxide, $\{Bu^tOBe(thf)\}_2O$, is formed, and pyridine gives $\{Bu^tOBe(py)\}_2O$. The pentane-2,4-dionato-complex, $\{Bu^tOBe(C_5H_7O_2)\}_2$, is formed from the diketone and either Bu^tOBeBH_4 or Bu^tOBeMe. Reaction of pentane-2,4-dione with t-butoxyberyllium tetrahydroborate appears to proceed by two competing paths, one leading to the pentane-2,4-dionate mentioned above and the other to reduction of the dione giving 4,6-dimethyl-1,3,2-dioxaborinan, which was also synthesised from diborane and either pentane-2,4-dione or pentane-2,4-diol.

ALKOXYMETAL TETRAHYDROBORATES have been the subject of only a few studies. Several alkoxyaluminium tetrahydroborates have been prepared by the addition of diborane to alkoxylalanes. Their association, generally to dimers or dimer–trimer equilibria, was attributed to AlO_2Al bridges, with no AlH_2B bridges.[1] Some trimethylsiloxyaluminium tetrahydroborates have been obtained from the corresponding chlorides and lithium tetrahydroborate.[2] On the basis of ^{11}B n.m.r. and i.r. evidence the dimer, $\{(BH_4)_2AlOSiMe_3\}_2$, for example, is believed to contain six-co-ordinate aluminium and both AlO_2Al and AlH_2B bridges. We now describe a few

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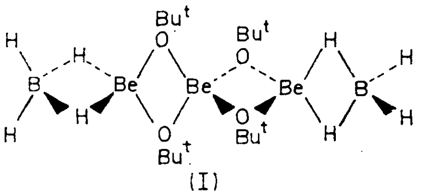
[1] H. Nöth and H. Stuchy, *Z. anorg. Chem.*, 1968, **358**, 441.

[2] B. Armer and H. Schmidbauer, *Chem. Ber.*, 1968, **101**, 2256.

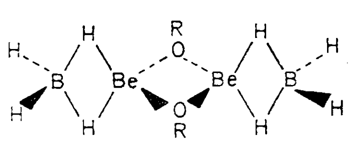
alkoxyberyllium tetrahydroborates all of which were obtained from the analogous alkoxyberyllium chlorides,[3,4] in most cases as ether complexes, and lithium tetrahydroborate. The butoxyberyllium chloride, $Cl_2Be_3(OBu^t)_4$,[3] whose crystal structure has been determined,[5] has a straight chain of three butoxy-linked beryllium atoms and yielded the tetrahydroborate believed to have structure (I). This is the only alkoxyberyllium tetrahydroborate we have found to be monomeric in benzene.



(I)

Like the other compounds described below the i.r. spectral characteristics of (I) in the 2000—2600 cm^{-1} region are very similar to those of crystalline beryllium tetrahydroborate[6] which, in the solid state, has bidentate tetrahydroborate groups with BH_2Be bridges.[7] The rather high melting point (245—247°) of (I) is consistent with its proposed highly symmetrical structure. A preliminary crystallographic study of (I) by Dr. J. Howatson of this department has indicated that the space group is $C_{2/c}$ or C_c.

t-Butoxyberyllium chloride, as the ether complex $(Bu^tOBeCl,OEt_2)_2$ gives, in diethyl ether, a tetrahydroborate Bu^tOBeBH_4 which, like the other alkoxyberyllium tetrahydroborates crystallises without complexed ether. In contrast, the same complex yields only $\{Bu^tOBeCl(thf)\}_2$ when the same reaction is attempted using tetrahydrofuran (thf) as solvent. Though t-butoxyberyllium tetrahydroborate is too sparingly soluble in benzene to allow cryoscopic molecular-weight measurement, we believe it is dimeric like its more soluble analogues $(Me_2EtCOBeBH_4)_2$ and $(Et_3COBeBH_4)_2$. Both on account of their i.r. spectra in the 2000—2600 cm^{-1} region,[8] and because they do not complex with ether or tetrahydrofuran (*i.e.* the metal is likely already to be four-co-ordinate) we believe these tetrahydroborates have structure (II). A co-ordination number greater than four has been observed for beryllium only when all the ligands are hydrogen atoms, as in crystalline $Be(BH_4)_2$.[7]



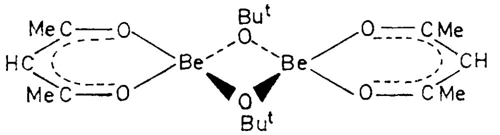
(II)

Although hydrolysis of (I) gave all the hydridic hydrogen as hydrogen gas, we were surprised to find that hydrolysis of (II; R = Bu^t, Me_2EtC, Et_3C) produced only about half the theoretical hydrogen, even in the presence of dilute sulphuric acid, but attempts to isolate a reaction intermediate (*i.e.* a product of partial hydrolysis) were not successful.

t-Butoxyberyllium tetrahydroborate did not react with several olefins, even at elevated temperatures (details are given in the Experimental section), nor did it react with acetone, di-t-butyl ketone or benzophenone in toluene solution: the tetrahydroborate was recovered in all cases. Benzophenone is reduced by (II; R = Bu^t) in the presence of ether. The reaction intermediate is only sparingly soluble in benzene and was not investigated, except for hydrolysis which gave diphenylmethanol in 90% yield.

With the intention of preparing an isopropoxy-derivative, we allowed t-butoxyberyllium tetrahydroborate to react with acetone in tetrahydrofuran. To our surprise we isolated the monomeric alkoxyberyllium oxide, $\{Bu^tOBe(thf)\}_2O$, in low yield. The same product was isolated when we allowed t-butoxyberyllium tetrahydroborate to react with di-t-butyl ketone in tetrahydrofuran. This result suggested to us that the ketone was the source of oxide-oxygen, so, in the case of acetone, propene or a higher olefin should be formed. However, a small amount of hydrogen was the only volatile material detected. We are unable to account for this transformation. Pyridine, as expected, replaces tetrahydrofuran giving $\{Bu^tOBe(py)\}_2O$. The oxide, along with bis(2,6-di-t-butylphenoxy)beryllium,[4] are the only known monomeric alkoxides of beryllium.

Since acetylacetonato-complexes are among the most volatile metal complexes known, the reaction of pentane-2,4-dione with t-butoxyberyllium tetrahydroborate in toluene was studied. The product, isolated in 50% yield, is dimeric t-butoxyberylliumpentane-2,4-dionate, also prepared from methylberyllium t-butoxide[9] and the diketone. The structure of the dimer is likely to be (III),



(III)

with bridging butoxide groups having three-co-ordinate oxygen atoms rather than terminal two-co-ordinate butoxide groups. The butoxide group is replaced by pentane-2,4-dione giving acetylacetonatoberyllium.[10] That compound (III) is a dimer, in contrast to the trimeric methoxy- and ethoxy-analogues,[11] is undoubtedly due to the large size of a t-butoxy- relative to an ethoxy-group. Replacement of a tetrahydroborate by an

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[3] R. A. Andersen, N. A. Bell, and G. E. Coates, *J.C.S. Dalton*, 1972, 577.

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

[5] H. M. M. Shearer and J. Twiss, personal communication.

[6] J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, 1971, **54**, 5257.

[7] D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, 1972, **11**, 820.

[8] T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, 1972, **11**, 2540.

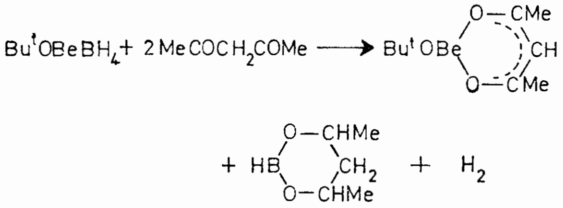
[9] G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1968, 477.

[10] C. L. Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 721.

[11] R. M. Klein and J. C. Bailar, *Inorg. Chem.*, 1963, **2**, 1187.

acetylacetonate is not unique, as acetylacetonatobis(triphenylphosphine)copper is formed from $(Ph_3P)_2CuBH_4$ and acetylacetone.[12]

To determine what volatile materials were formed, Bu^tOBeBH_4 and acetylacetone were allowed to react in a vacuum system. Hydrogen (0·58 mmol for each mmol of tetrahydroborate) and 4,6-dimethyl-1,3,2-dioxaborinan were the only two volatiles produced. The alkoxyborane was also prepared from diborane and the diketone, and from diborane and the diol. Thus, the



rate of reduction of the β-diketone (forming the alkoxyborane) and the rate of acetylacetonation (forming the acetylacetoxyberyllium alkoxide) are similar. Since pentane-2,4-dione is largely an enol, the reaction may be thought of as that of a protic acid with a tetrahydroborate. Indeed, reaction of t-butyl alcohol with t-butoxyberyllium tetrahydroborate in diethyl ether gave $Be(OBu^t)_2$ in 31% yield.

Pentane-2,4-diol was prepared by the sodium tetrahydroborate reduction of pentane-2,4-dione in 25% yield, the yield being increased by a factor of more than 2 when $LiAlH_4$ is used.[13] Though the ^1H n.m.r. spectrum of the diol in $CDCl_3$ is similar to that previously reported,[13] the spectrum in benzene solution is considerably different (details are given in the Experimental section). The major difference is the appearance of two hydroxyl proton resonances in an area ratio of 1 : 1·6. Since the diol is a diastereoisomer, *meso*- and (±)-conformations are possible, each having the hydroxy-groups in two different environments relative to each other, *viz. trans* and *gauche*, in a 1 : 2 area ratio.

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[14] method under standard conditions. Boron was determined volumetrically by the mannitol method.[15] 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. ^1H N.m.r. spectra were recorded by use of a Varian HA-100 spectrometer, with benzene as solvent and internal reference (τ 2·73) unless otherwise specified. Many of the compounds described below decompose when heated without melting. In such cases the main i.r. absorptions are quoted for characterisation; these were recorded as Nujol mulls. Most of the products 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 not in general recorded. Except where noted, yields were, apart from transfer losses, nearly quantitative.

Tetra-t-butoxytriberyllium Bistetrahydroborate, $(BH_4)_2Be_3(OBu^t)_4$.—Lithium tetrahydroborate (0·18 g, 0·0082 mol) in tetrahydrofuran (10 ml) was added to $Cl_2Be_3(OBu^t)_4$ (1·63 g, 0·0041 mol) in tetrahydrofuran (20 ml) and the mixture was stirred for 30 min; the tetrahydrofuran was removed under reduced pressure, benzene (20 ml) was added, and the suspension was stirred for 15 min. The solution was filtered and the benzene was removed under reduced pressure from the filtrate to give a white solid which gave colourless *needles* from benzene (yield 0·69 g, 48%), m.p. 245—247°. The compound sublimed at 100—110°/10^{-2} mmHg [Found: hydrolysable hydrogen, 2·3; Be, 7·8; t-butoxy, 82·9%; *M* (cryoscopically, 0·72 and 0·49% w/w in benzene), 322 and 324. $C_{16}H_{44}Be_3B_2O_4$ requires hydrolysable hydrogen, 2·3; Be, 7·9; t-butoxy, 83·7%; *M*, 349]; $\nu_{max.}$ (between 1500 and 2500 cm^{-1}) 2485s, 2435m, 2285w, 2265w, 2195w, 2133s, 2095m, 2015w, and 1521m cm^{-1}.

t-Butoxyberyllium Tetrahydroborate.—Lithium tetrahydroborate (0·16 g, 0·0070 mol) in diethyl ether (20 ml) was added to the diethyl ether complex of chloro-t-butoxyberyllium (1·35 g, 0·0070 mol) in diethyl ether (30 ml). The ether boiled during the addition and a precipitate formed. The suspension was stirred for 30 min after which volatile material was removed under reduced pressure at −30 to −40°; the white solid residue was stirred for 15 min with toluene (20 ml). The solution was filtered, toluene was removed from the filtrate under reduced pressure, and the white solid was crystallised from benzene to give *prisms* (0·27 g, 40%). When heated in a sealed capillary, the compound became transparent at *ca.* 185° and did not melt to 300°, though it sublimed at 60—70°/10^{-2} mmHg (Found: hydrolysable hydrogen, 1·9; t-butoxy, 74·0; Be, 9·4. $C_4H_{13}BeBO$ requires hydrolysable hydrogen, 4·1; t-butoxy, 75·3; Be, 9·3%); $\nu_{max.}$ 2485, 2435s, 2275w, 2265w, 2135s, 2110s, 2105w, and 1525m cm^{-1}. The tetrahydroborate was not sufficiently soluble in benzene for its molecular weight to be measured cryoscopically.

When tetrahydrofuran was used as solvent rather than diethyl ether, $\{ClBeOBu^t(thf)\}_2$ was isolated, m.p. 174—176° (decomp.) [lit.,[3] 175—177° (decomp.)].

1,1-*Dimethylpropoxyberyllium Tetrahydroborate*, $(Me_2EtCOBeBH_4)_2$.—This compound was similarly prepared from lithium tetrahydroborate (0·22 g, 0·010 mol) in diethyl ether (20 ml) and $Me_2EtCOBeCl$, prepared from $BeCl_2,2OEt_2$ (1·2 g, 0·0050 mol) and $(Me_2EtCO)_2Be$[4] (0·92 g, 0·0050 mol) in diethyl ether (30 ml). The tetrahydroborate crystallised from toluene (−78°) as *cubes*. When heated in a sealed capillary the compound softened at *ca.* 40° and melted at 128—131° [Found: hydrolysable hydrogen, 1·3; Me_2EtCO, 77·6; Be, 8·0%; *M* (cryoscopically, 0·50 and 0·33% w/w in benzene), 219 and 220. $C_{10}H_{30}Be_2B_2O_2$ requires hydrolysable hydrogen, 3·6; Me_2EtCO, 78·4; Be, 8·1%; *M*, 222]; $\nu_{max.}$ 2482s, 2440s, 2278w, 2200w,sh, 2115s, 2095s, 2015w,sh, and 1528m cm^{-1}.

1,1-*Diethylpropoxyberyllium Tetrahydroborate*, $(Et_3COBeBH_4)_2$.—This compound was similarly prepared from

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[12] F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 3.

[13] J. W. Frankenfeld and W. E. Tyler, *J. Org. Chem.*, 1971, **36**, 2110.

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

[15] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, 'Applied Inorganic Analysis,' John Wiley, New York, 1953, p. 753.

lithium tetrahydroborate (0·22 g, 0·010 mol) in diethyl ether (20 ml) and 1,1-diethylpropoxyberyllium chloride–diethyl ether complex, prepared from $BeCl_2,2OEt_2$ (1·2 g, 0·0050 mol) and $(Et_3CO)_2Be$ [4] (1·2 g, 0·0050 mol) in diethyl ether (30 ml). The tetrahydroborate was crystallised from hexane (−78°) as colourless *needles*, m.p. 42—44° [Found: hydrolysable hydrogen, 1·9; Et_3CO, 81·7; Be, 6·5%; *M* (cryoscopically, 0·89 and 0·60% w/w in benzene), 289 and 275. $C_{14}H_{38}Be_2B_2O_2$ requires hydrolysable hydrogen, 2·9; Et_3CO, 82·8; Be, 6·5%; *M*, 278]; $\nu_{max.}$ 2510s, 2450s, 2270w, 2115s, 2070s, 2010w, and 1536m cm^{-1}.

Bis[*t-butoxy*(*tetrahydrofuran*)*beryllium*] *Oxide*, $\{Bu^tOBe(thf)\}_2O$.—Acetone (1·1 g, 0·018 mol) in tetrahydrofuran (5 ml) was added to Bu^tOBeBH_4 (0·88 g, 0·0091 mol) in tetrahydrofuran (15 ml). The solution became warm, *ca.* 40°. After the addition the solution was stirred for 15 min, the tetrahydrofuran was removed under reduced pressure: the white residue crystallised as *prisms* from hexane–benzene (3 : 1) (1·1 g, 35%). When heated, it shrank at *ca.* 105°, turned brown at 210°, and did not melt to 300° [Found: Be, 5·3%; *M* (cryoscopically, 1·14 and 0·86% w/w in benzene), 335 and 339. $C_{16}H_{34}Be_2O_5$ requires Be, 5·6%; *M*, 324]. The ratio of t-butyl alcohol to tetrahydrofuran (1 : 1) was indicated by hydrolysis of a solution of the compound in benzene and the recording of its ^1H n.m.r. spectrum. The ^1H n.m.r. spectrum of the oxide showed the following signals τ 5·88 (m, β-CH_2 of thf), 8·50 (s, Bu^tOBe), and 8·63 (α-CH_2 of thf) (area ratio 3·8 : 9 : 4·2); $\nu_{max.}$ 1375s, 1245m, 1195m, 1165m, 1135w, 1018s, 960s, 912w, 875m, 855w, 798m, 765s, 710w, 685w, 670w, 593s, and 475w cm^{-1}.

The oxide was also obtained from Bu^t_2CO and Bu^tOBeBH_4 in a 2 : 1 molar ratio in thf, as shown by its decomposition temperature, and i.r. and ^1H n.m.r. spectra.

In an experiment done on a vacuum line, acetone (91·5 mg, 1·58 mmol) and tetrahydrofuran (115 mg, 1·60 mmol) were added to Bu^tOBeBH_4 (73 mg, 0·75 mmol) at −196°. The solid was warmed to room temperature and stirred for 2 h. The volatile materials were fractionated through a −196° trap, giving hydrogen (0·14 mmol). No gas was obtained from the −196° trap when fractionated through a −95° trap. The contents of the −95° trap were condensed onto Me_2Mg (118 mg, 2·19 mmol) at −196° and stirred at room temperature for 30 min. However, no volatile matter was obtained when its contents were fractionated through a −31° trap.

Bis{*t-butoxy*(*pyridine*)*beryllium*} *Oxide*, $\{Bu^tOBe(py)\}_2O$.—This complex was obtained by displacement of tetrahydrofuran from the preceding complex by pyridine, and crystallised as colourless *prisms* from benzene. When heated in a sealed capillary it shrank at *ca.* 220°, turned brown at *ca.* 270°, and did not melt [Found: t-butoxy, 42·5; pyridine, 47·2; Be, 5·2%; *M* (cryoscopically, 1·00 and 0·75% w/w in benzene), 355 and 362. $C_{18}H_{28}Be_2N_2O_3$ requires t-butoxy, 43·2; pyridine, 46·8; Be, 5·3%; *M*, 338]; $\nu_{max.}$ 3130w, 3100w, 3080w, 3050w, 1615m, 1572w, 1490w, 1375m, 1245m, 1230m, 1215m, 1195w,sh, 1165m, 1150m, 1137m, 1058s, 1048s, 970s, 853w, 763s, 701s, 678s, 635w, 585s, and 470w cm^{-1}.

t-Butoxy(*pentane*-2,4-*dionato*)*beryllium* $(Bu^tOBeO_2C_5H_7)_2$.—*From t-butoxyberyllium tetrahydroborate and pentane*-2,4-*dione*. Pentane-2,4-dione (1·0 g, 0·010 mol) in toluene (10 ml) was added to Bu^tOBeBH_4 (0·97 g, 0·010 mol) in toluene (20 ml) at −78°. The solution was slowly warmed to room temperature, stirred for 15 min, and the volatiles were removed under reduced pressure to give a white solid which crystallised from toluene–hexane (3 : 2) as colourless *needles* (0·91 g, 50%). When heated, the compound shrank at *ca.* 150° and melted at 189—191° [Found: Be, 4·9%, *M* (cryoscopically, 1·40 and 1·06% w/w in benzene), 374 and 367. $C_{18}H_{32}Be_2O_6$ requires Be, 5·0%; *M*, 362]; $\nu_{max.}$ 1595s and 1532s cm^{-1}; τ 4·51 (s, MeCOC*H*), 8·15 (s, *Me*COCH), and 8·62 (s, *Bu*^{t}OBe) (area ratio 1 : 6 : 9).

From methyl-t-butoxyberyllium. Pentane-2,4-dione (1·4 g, 0·014 mol) in diethyl ether was added to methyl-t-butoxyberyllium [9] (1·3 g, 0·014 mol) in diethyl ether (30 ml) at −78°. After addition, the solution was warmed to room temperature, stirred for 15 min, and the volatiles were removed under reduced pressure to yield a white solid which crystallised as *needles* from benzene, shown to be $Bu^tOBeO_2C_5H_7$ by their m.p. 186—188°.

Dipentane-2,4-*dionatoberyllium*.—An excess of pentane-2,4-dione was added to pentane-2,4-dionato-t-butoxyberyllium (1·0 g, 0·0053 mol) in toluene (10 ml) at room temperature. After the addition, the solution was stirred for 1 h, the volatile matter was removed under reduced pressure, and the resulting white solid was crystallised from hexane–benzene (3 : 1) to give needles. The needles were shown to be dipentane-2,4-dionatoberyllium by their m.p. 105—106° (lit.,[10] 108°).

Reaction of t-Butoxyberyllium Tetrahydroborate and Pentane-2,4-*dione in a Vacuum line*.—1 : 1 *Molar ratio*. t-Butoxyberyllium tetrahydroborate (87 mg, 0·90 mmol) and pentane-2,4-dione (89·8 mg, 0·898 mmol) were stirred together in a flask connected to a vacuum line for 1 h. The volatiles were fractionated through a −196° trap, giving hydrogen (0·52 mmol), and a −31° trap giving 4,6-dimethyl-1,3,2-dioxaborinan, whose vapour pressure was 12·5 mm at 22°. The i.r. and ^1H n.m.r. spectra were identical to that of an authentic sample prepared as described below.

1 : 2 *Molar ratio*. The tetrahydroborate (84 mg, 0·87 mmol) and the β-diketone (173·5 mg, 1·735 mmol) were mixed, and the volatile products were characterised as above, giving hydrogen (0·77 mmol) and the alkoxyborane.

4,6-*Dimethyl*-1,3,2-*dioxaborinan*.—*From diborane and pentane*-2,4-*dione*. Diborane (78·6 ml,* 3·51 mmol) was condensed on pentane-2,4-dione (293·6 mg, 2·936 mmol) at −196°. As the solid was warmed to room temperature, bubbles were visible at *ca.* −50°. At room temperature the liquid was yellow. The diborane was recondensed at −196° and then warmed through three cycles, at which time the yellow colour disappeared. Fractionation through a −196° trap gave hydrogen (37·2, 1·66 mmol), through a −112° trap gave diborane (51·5 ml,* 2·30 mmol), and through a −31° trap gave the dioxaborinan as a viscous colourless liquid at that temperature (Found: hydrolysable hydrogen, 0·87; B, 9·6. $C_5H_{11}BO_2$ requires hydrolysable hydrogen, 0·88; B, 9·7%). The diol formed on hydrolysis was shown to be pentane-2,4-diol by comparison of its ^1H n.m.r. spectrum in $CDCl_3$ to that of the diol prepared as described below. The dioxaborinan had the following spectral features: $\nu_{max.}$ (gas phase): 2980s, 2925m, 2560s, 2500m, 1400s, 1345m, 1280s, 1215s, 1150w, 973w, 885m, 780w, 720w, and 488w cm^{-1}; τ 6·13 [m, MeC*H*(OH)CH_2], 8·70 [m, MeCH(OH)C*H*$_2$], 8·90 (d) and 8·97 (d) [each *J* 2 Hz, *Me*CH(OH)C*H*$_2$] (area ratio 1 : 1 : 3).

From diborane and pentane-2,4-*diol*. Diborane (9·85 ml,* 0·435 mmol) was condensed on pentane-2,4-diol (93·0 mg, 0·894 mmol) at −196° and treated as above. Fractionation gave only hydrogen (3·98 ml,* 0·178 mmol) and

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* Normalised to s.t.p.

4,6-dimethyl-1,3,2-dioxaborinan, identified by its i.r. and ^{1}H n.m.r. spectra.

Pentane-2,4-*diol*.—Pentane-2,4-dione (10·0 g, 0·100 mol) in methanol (40 ml) was slowly added to sodium tetrahydroborate (7·6 g, 0·20 mol) in 0·001M-sodium hydroxide (20 ml) at 0°. After the addition the solution was stirred for 24 h at room temperature, water (20 ml) was added, and the diol was extracted with diethyl ether (3 × 30 ml) from a salt-saturated solution. The diethyl ether extracts were dried ($MgSO_4$), the diethyl ether was evaporated, and the resulting viscous liquid distilled at 74—75°/3 mmHg (lit.,[16] 198—199°), giving 2·6 g (25%) of the *diol*. The n.m.r. spectra showed the following signals: τ ($CDCl_3$/Me_4Si) 5·72 [s, MeCH(O*H*)CH$_2$], 5·94 [m, MeC*H*(OH)CH$_2$], 8·46 [m, MeCH(OH)C*H*$_2$], 8·78 (d) and 9·05 (d) [each *J* 2 Hz, *Me*CH(OH)CH$_2$] (area ratio 1 : 1 : 1 : 3); τ ($CHCl_3$/Me_4Si recorded at 60 MHz [13]) 5·21 [s, MeCH(OH)CH$_2$], 6·04 [m, MeC*H*(OH)CH$_2$], 8·49 [t, MeCH(OH)CH$_2$], 8·82 [d, *Me*CH(OH)CH$_2$]. The high field doublet of doublets observed at 100 MHz is undoubtedly due to the greater resolution at that frequency. The ^{1}H n.m.r. spectrum of the *diol* showed the following signals: τ (benzene at 100 MHz) 4·84 [d, *J* 2 Hz, MeCH(O*H*)CH$_2$], 5·14 [d, *J* 2 Hz, MeCH(O*H*)CH$_2$], 5·75 [m, MeC*H*(OH)CH$_2$], 8·33 [m, MeCH(OH)C*H*$_2$], and 8·41 [m, MeCH(OH)CH$_2$], 8·68 and 8·77 [a pair of overlapping doublets appearing as a triplet, *J* 6 Hz, *Me*CH(OH)CH$_2$]. The area ratio of the low field doublets attributed to the hydroxyl protons (which disappear on addition of D_2O) is 1 : 1·6.

Reactions of t-Butoxyberyllium Tetrahydroborate.—*With olefins*. But-1-ene (0·96 g, 0·017 mol) and Bu^{t}OBeBH$_4$ (0·83 g, 0·0086 mol) were stirred in toluene (10 ml) for 1 h. Removal of volatile matter under reduced pressure yielded a solid which gave prisms from benzene; these were shown to be of the unchanged tetrahydroborate by i.r. spectroscopy. Replacement, in the above scheme, of toluene by tetrahydrofuran gave a similar result, as did reaction of 2,3-dimethylbut-2-ene and the tetrahydroborate in tetrahydrofuran. Dec-1-ene (0·59 g, 0·0047 mol) and Bu^{t}OBeBH$_4$ (0·23 g, 0·0024 mol) were refluxed in toluene (15 ml) for 4 days. After removal of volatile matter under reduced pressure the resulting solid was crystallised from benzene to give prisms shown to be the unchanged tetrahydroborate by its i.r. spectrum.

With acetone. Acetone (0·67 g, 0·012 mol) was added to Bu^{t}OBeBH$_4$ (1·1 g, 0·012 mol) in toluene (25 ml). After addition the solution was stirred for 15 min, volatile matter was removed under reduced pressure, and the white residue was crystallised from benzene. The compound was shown to be the tetrahydroborate from its infrared spectrum.

With 2,2,4,4-*tetramethylpentan*-3-*one*. The ketone (0·36 g, 0·025 mol) and the tetrahydroborate (1·2 g, 0·013 mol) were stirred for 15 min in toluene (25 ml). After removal of the volatile matter under reduced pressure, the residue was crystallised from benzene and shown to be Bu^{t}OBeBH$_4$ by its i.r. spectrum.

With benzophenone. The ketone (1·6 g, 0·0091 mol) and the tetrahydroborate (0·88 g, 0·0091 mol) were stirred in toluene (30 ml) for 30 min. Removal of volatile material under reduced pressure gave a solid which was crystallised from benzene and shown to be unchanged tetrahydroborate by its i.r. spectrum.

With benzophenone in diethyl ether. The ketone (4·1 g, 0·022 mol) was added to Bu^{t}OBeBH$_4$ (1·1 g, 0·012 mol) in diethyl ether (30 ml). After addition, the solution was stirred for 15 min, and the volatile matter removed under reduced pressure, yielding a sticky white solid which was sparingly soluble in benzene. Hydrolysis gave diphenylmethanol (3·6 g, 90%), m.p. 68° (lit.,[17] 67°).

With t-butyl alcohol in diethyl ether. The alcohol (0·37 g, 0·0051 mol) was added to Bu^{t}OBeBH$_4$ (0·25 g, 0·0026 mol) in diethyl ether (10 ml). After addition, and after 15 min with stirring, evaporation of volatile material left a residue which crystallised from hexane (−5°) as prisms, m.p. 110°, whose i.r. spectrum was identical to that of [Be(OBu^t)$_2$]$_3$, yield 0·12 g, 31% (lit.,[9] m.p. 112°).

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[16] A. Franke and M. Kohn, *Chem. Ber.*, 1904, **37**, 4730.

[17] W. Tschelinzeff, *Chem. Ber.*, 1904, **37**, 4539.