NOVEL COMPLEXES OF AMIDES AND OTHER SPECIES WITH A HETEROCYCLIC BORON BETAINE.[1]

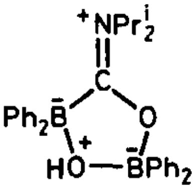
Andrew S. Fletcher, Walter E. Paget and Keith Smith.*

Department of Chemistry, University College of Swansea, Swansea SA2 8PP, U.K.

Abstract - The heterocyclic boron-containing betaine (1) forms stable 1:1 addition complexes with water, amines and, more surprisingly, simple amides.

INTRODUCTION

We have previously reported that reaction of diphenylbromoborane with di-isopropylcarbamoyl-lithium, followed by treatment with water and chromatography on silica gives the novel heterocyclic betaine (1) in almost quantitative yield.[2]



(1)

Prior to chromatography the product was a crude yellow viscous oil with broad i.r. bands at 3200 cm^{-1} (weak), 1650 cm^{-1} (strong) and sharp bands at 1620 cm^{-1} (s) and 1580 cm^{-1} (s). This contrasts markedly with (1), for which the characteristic bands are the sharp absorptions at 3550 cm^{-1} (medium) and 1580 cm^{-1} (s). By dissolving the crude product in benzene and careful crystallization large prismatic crystals were obtained. We now report the identification of this product as a 1:1 complex of (1) with di-isopropylformamide (DIPF). We also wish to report that complexation of (1) is fairly general for other simple amides as well as for amines and water.

RESULTS AND DISCUSSION

A crude product was obtained by reacting diphenylbromoborane with diisopropylcarbamoyl-lithium (-78°C rising to room temperature), treatment with water, extraction into ether and removal of the solvent. The heavy viscous oil was dissolved in benzene which was concentrated by distillation and then allowed to cool slowly to produce large prismatic crystals.

The i.r. spectrum (KBr disc) of these crystals revealed no sharp band at 3550 cm^{-1} (characteristic of (1)), but showed a very broad, weak band in the region 2800-2300 cm^{-1}. It also showed a sharp, intense absorption at 1620 cm^{-1} and a $C{=}N^+$ absorption similar to that of (1) at 1580 cm^{-1}.

The ^{1}H n.m.r. spectrum ($CDCl_3$) contained signals at $\delta = 7.2$ p.p.m. (ca. 22H, complex multiplet, but showing separation into two groups in the ratio ca. 2:3); 4.00, 3.71, 3.42 and 3.00 (each signal 1H, septet, J = 7Hz); and 1.52, 0.96, 0.86 and 0.64 p.p.m. (each signal 6H, doublet, J = 7Hz). In later samples prepared by another method (see below) two additional signals separated from the aromatic resonances. One was exchangeable; the other showed variation in chemical shift, sometimes occurring as high as 6.4 p.p.m. The ^{11}B n.m.r. spectrum was virtually identical to that of (1).

The ^{13}C n.m.r. spectrum ($CDCl_3$) showed signals due to four different isopropyl groups (δ = 19.14, 19.84, 20.89, 22.67 p.p.m., all quartets in the off-resonance decoupled mode; 44.33, 47.21, 47.75, 52.71 p.p.m., all doublets in the off-resonance mode), two of which correspond closely to those of (1), and signals due to two different sets of phenyl resonances (δ = 125.71, 126.08 p.p.m., para-carbons; 126.68, 127.08 p.p.m., meta-carbons; 132.40, 134.58 p.p.m., ortho-carbons; ca. 148, 150 p.p.m., broad, weak, ipso-carbons). Additionally, the immonium carbon atom which is present in (1) appeared as a weak broad signal at ca. 200 p.p.m. and there was a carbonyl signal at 162.63 p.p.m. Significantly, this last signal was a doublet in the off-resonance decoupled spectrum showing that the *formyl hydrogen atom of the DIPF unit was present. The formyl* proton was not observed as a separate signal in the initial ^{1}H n.m.r. spectrum, but its location was verified by on-resonance decoupling of the aromatic protons, which caused the ^{13}C n.m.r. signal for the carbonyl carbon atom to collapse to a singlet.

These data appeared to indicate that the product was a 1:1 complex between (1) and DIPF, a highly surprising result in view of the structure of (1). Further support was obtained from the field desorption mass spectrum,[3] which showed substantial peaks at m/e 604 (ion corresponding to (1) + $Pr^{i}_{2}NCHO$), 475 (loss of $Pr^{i}_{2}NCHO$), and 398 (further loss of Ph). Simple confirmation of this structure was achieved by mixing equimolar amounts of (1) and DIPF in ether, whereupon an identical complex crystallized spontaneously on evaporation.

In view of the surprising ability of (1) to form a stable, crystalline 1:1 complex with DIPF we have investigated its ability to complex other compounds. Compound (1) and the appropriate substrate were mixed in a 1:1 ratio in ether and the solvent removed at room temperature. Complex formation was indicated by a significant change in the nature of the O-H stretching frequency in the i.r. spectrum, particularly in the disappearance of the band at 3550 cm^{-1} (see above), and the appearance of broad bands at lower frequency. The solid adduct was then dissolved in boiling ether-hexane and allowed to crystallize, if possible.

The compounds fall into three categories: a) those which, like DIPF, form stable recrystallizable complexes with (1); b) those which form distinct solid adducts, as revealed by change of the O-H absorption in the i.r. spectrum, but for which the adducts are not sufficiently stable to allow recrystallization from boiling solvents and c) those for which the i.r. spectrum of the 1:1 mixture is merely the sum of the separate spectra of (1) and the compound, indicating little or no complex formation. The table summarizes the results.

Table

a)	Compounds forming stable recrystallizable complexes with (1)	$Pr^{i}_{2}NCHO$; Me_2NCHO; CH_3CONH_2; $CH_3CONHMe$; CH_3CONMe_2; *c*-$C_6H_{11}NH_2$; $PhCH_2NH_2$; H_2O.
b)	Compounds forming complexes which cannot be recrystallized from boiling ether-hexane.	$PhCONH_2$; $CH_3CONHPh$; (*c*-$C_6H_{11})_2NH$; $Pr^{i}_{2}NH$.
c)	Compounds which do not complex (1)	CH_3CN; $ClCH_2CN$; CH_3CO_2Et; $PhCO_2Et$; N-benzoylleucine methyl ester; N-benzoylvalyl-valine methyl ester.

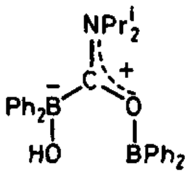
Nitriles and esters show no evidence for complexation with (1) in contrast to simple amides and amines which form strong complexes. Complexes of amines and amides which are relatively hindered at the site of co-ordination (oxygen for amides - see below) are relatively weak and cannot be recrystallized. Indeed, the even more hindered amino acid amide derivatives tested showed no evidence for complex formation.

The melting behaviour of all of the crystallizable complexes is similar. They either first melt at *ca.* 100°C and then rapidly crystallize again or change their crystal shape during heating, finally melting close to the melting point of (1) (179°C). This could be consistent with loss of the co-ordinating molecule by evaporation during heating. The transition temperature depends on the rate of heating, and is not easily reproducible.

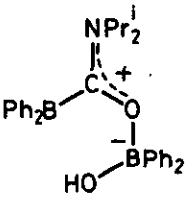
The boron atoms in (1) in both the solid state (as indicated by preliminary X-ray analysis[2]) and in solution (^{11}B n.m.r.[2]) are co-ordinatively saturated. Thus, complex formation, especially from relatively poor donors such as amides, is rather unusual. However, adduct formation could occur in one of two ways: a) proton transfer from (1) to the donor to give a salt; or b) opening of the heterocyclic ring of (1) to give one boron atom in a 3-co-ordinate state capable of complexation; the other boron atom would remain as a hydroxyborate. There is no evidence to suggest that (1) is in any way acidic, and the changes in the spectra of DIPF induced by its complexation with (1) are totally different to those induced by its reactions with trifluoroacetic, sulphuric or methanesulphonic acids. We therefore discount mechanism (a). The changes induced by complexation of DIPF with boron acceptors such as diphenylbromoborane show some similarity, but even here there are substantial differences. For example, the large upfield shift (ca. 1.8 p.p.m.) of the formyl proton on complexation of DIPF with (1) is not matched on complexation with other acceptors. However, this can be rationalised by assuming complexation via the amide carbonyl oxygen to one of the boron atoms of (1) (see below).

Complexation of DIPF through oxygen is indicated by the following observations: a) the carbonyl stretching frequency is lowered on complexation; b) the isopropyl group methyl signals fail to coalesce at temperatures (50°C in $CDCl_3$, 120°C in chlorobenzene) for which the free amide signals have already coalesced, indicating increased C-N double bond character in the complex.

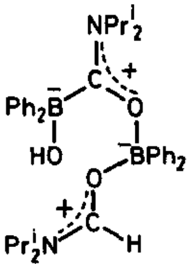
It is possible that (1) is in equilibrium with open-chain forms (2) and (3) in solution, providing two possible sites for coordination. However, models indicate that complexation of DIPF to the three-coordinate boron atom of (3) would be severely hindered, and we therefore favour complexation to (2) giving the complex (4).



(2)



(3)



(4)

The models also reveal that the formyl proton in complex (4) must lie within the shielding zone of one of the four phenyl rings in whatever conformation it adopts. This could account for the large upfield shift of this proton. By contrast, the formyl carbon atom sits at the edge of, or just outside, this zone and is affected much less.

It is interesting that a sample of the complex which was freshly prepared from dried (1) and dry DIPF showed a formyl proton resonance at δ = 6.4 p.p.m.; it is also interesting that addition of either D_2O or excess DIPF shifted this resonance downfield. *Evidently there is a* rapid equilibrium between free and complexed amide, leading to an averaged signal, and water also *competes with DIPF for complexation of (1). Indeed,* water slowly displaces DIPF or other amides from their complexes with (1) on exposure of the complexes to moist air. Attempts to form an ammonia complex by reaction of (1) with concentrated ammonia solution always resulted in the water complex. Nevertheless, water is easily removed from the complex by passage through a column of dry silica or by azeotropic distillation. Passage over silica also regenerates (1) from other complexes.

In conclusion, the boron-containing betaine (1) forms co-ordination complexes with amides, amines and water which are both unusual and interesting. The upfield shift of the formyl proton of DIPF (or DMF) when complexed to (1) is exceptionally large, but can be explained by its being forced to occupy a position directly over the shielding cone of one of the phenyl rings.

ACKNOWLEDGEMENT We thank the S.R.C. for a studentship (to A.S.F.) and a fellowship (to W.E.P.).

DEDICATION We dedicate this communication to Professor Herbert C. Brown, whose contributions to boron chemistry and to the study of boron complexes are unparallelled, on the occasion of his seventieth birthday.

REFERENCES

1. Part 8 in the series "Novel Heterocyclic Systems". For part 7, see I. Matthews, K. Smith J.R. Turner and G.E. Martin, *Heterocycles*, preceding publication.
2. A.S. Fletcher, W.E. Paget, K. Smith, K. Swaminathan, J.H. Beynon, R.P. Morgan, M. Bozorgzadeh and M.J. Haley, *J.Chem.Soc.*, *Chem.Comm.*, 1979, 347.
3. We thank Dr. D. Games of University College, Cardiff for running the spectrum for us.

Received, 21st September, 1981