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CARBON–BORON BOND CLEAVAGE BY AMINO ACIDS: AN IMPROVED ROUTE TO MIXED ANHYDRIDES OF DIPHENYLBORINIC AND AMINO ACIDS

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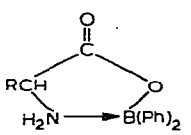
SUMMARY

The carbon–boron bonds of tetraphenylborate anion are sequentially cleaved by amino acids to yield diphenylborinic acid which, under the conditions of the reaction, is intercepted by the amino acid present to yield the corresponding mixed anhydride of diphenylborinic acid and the amino acid, in good yield. The reaction is sufficiently general to constitute a convenient *in situ* process for the preparation of these B←N coordination stabilized compounds.

INTRODUCTION

There is considerable current interest in the physical and chemical properties of compounds containing an intramolecular B–N coordination site[1]. Esters[2] and anhydrides[3] of borinic acids passes a remarkable degree of hydrolytic and oxidative stability when internal B–N coordination occurs. Zimmerman[4] has shown that a steric effect alone cannot account for the greatly increased hydrolytic stability of amino alcohol borinates when compared to boron esters of ordinary alcohols[5]. Anhydrides of amino acids and borinic acid (I) similarly possess a high degree of hydrolytic stability[3].



(I)

Compounds (I) are also reported to have broad insecticidal, fungicidal and herbicidal activity[3] and to be effective against Helga and L-16 cells[6].

Two routes for the preparation of the mixed anhydride of diphenylborinic and amino acids are available. One reaction scheme requires butyl diphenylborinate[6] [eqn. (1)], an oxidatively unstable intermediate that requires prior preparation.

$$(Ph_2)BOBu + RCH(NH_2)CO_2H \rightarrow (I) + BuOH \quad (1)$$

The second route involves a carbon–boron bond cleavage reaction in xylene between triphenylborane and an amino acid[3] [eqn. (2)].

$$(Ph)_3B + RCH(NH_2)CO_2H \rightarrow (I) + PhH \quad (2)$$

Triphenylborane has very poor oxidation stability and, even more limiting, the reaction was found unsatisfactory with tyrosine and histidine.

RESULTS AND DISCUSSION

We now report a very convenient and satisfactory method for the preparation of (I) utilizing the significantly more stable[7] and commercially available sodium tetraphenylborate*, the appropriate amino acid and one equivalent of hydrochloric acid in water. The reaction requires prolonged (10–24 h) reflux in order that the various intermediate steps proceed to completion.

We believe that the reaction involves the following steps:

(*a*). Formation of the tetraphenylborate salt (II) of the amino acid hydrochloride [eqn. (3)];

$$NaB(Ph)_4 + [RCH(NH_3)CO_2H]^+ Cl^- \rightarrow \underset{(II)}{[(Ph)_4B]^-[RCH(NH_3)CO_2H]^+} \quad (3)$$

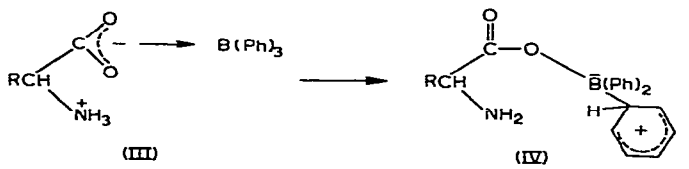
(*b*). Decomposition of (II) to triphenylborane, benzene and the amino acid [eqn. (4)];

$$(II) \rightarrow (Ph)_3B + PhH + RCH(NH_2)CO_2H \quad (4)$$

(*c*). Reaction between triphenylborane and the amino acid to produce (I) [eqn. (5)];

$$(Ph)_3B + RCH(NH_2)CO_2H \rightarrow (I) + PhH \quad (5)$$

Intermediate (II) is isolable but decomposes rapidly at room temperature. Triphenylborane can be isolated as the major boron containing decomposition product. A recommended method for the preparation of high quality triphenylborane is the pyrolyses of an acid ammonium salt of tetraphenylborate[8]. If (II) (slightly wet) is permitted to stand in a sealed container under nitrogen, it slowly converts in several days to (I). The reaction between triphenylborane and amino acid [eqn. (5)] in refluxing water also produces (I) in good yield. Since Ph_3B is rapidly cleaved to $(PhBO)_3$ and PhH in hot water[9], it is believed that step (*c*) proceeds through a coordination stabilized intermediate, possibly (III), followed by proton transfer and C–B cleavage:



Electrophilic attack by proton at C-1 of *B*-phenyl to yield a transient zwitterion analogous to (IV) was proposed by Cooper and Powell[10] from kinetic studies of protolysis of tetraphenylborate anion.

* Fisher Scientific Company.

EXPERIMENTAL

Glycinatodiphenyl borane

A mixture of 0.002 mole (0.15 g) glycine and 0.002 mole (0.68 g) sodium tetraphenylborate in 50 ml water was refluxed for 18 h. The reaction mixture was filtered, washed well with water, than benzene and dried to yield 0.28 g (60% yield) of a fine white powder m.p. 234°*, lit. 238°[6]. The product was identical with that obtained by the method of Lang, Nützel and Schubert[3]. (Found**: C, 69.83; H, 5.84; B, 4.78; N, 5.64. $C_{14}H_{14}BNO_2$ calcd.: C, 70.33; H, 5.90; B, 4.52; N, 5.86%.)

By the above general procedure, the following products were prepared:

DL-*Alaninatodiphenylborane*

M.p. 226°, 83% yield. (Found: C, 72.47; H, 6.53; B, 4.29; N, 5.10. $C_{15}H_{16}BNO_2$ calcd.: C, 71.18; H, 6.37; B, 4.27; N, 5.54%.)

DL-*Phenylalaninatodiphenylborane*

M.p. 219°, 85% yield. (Found: C, 76.97; H, 5.92; B, 4.52; N, 4.33. $C_{21}H_{20}BNO_2$ calcd.: C, 76.62; H, 6.12; B, 3.28; N, 4.25%.)

DL-*Prolinatodiphenylborane*

M.p. 272°, 70% yield. (Found: C, 73.00; H, 6.77; B, 4.06; N, 5.00. $C_{17}H_{18}BNO_2$ calcd.: C, 73.15; H, 6.50; B, 3.87; N, 5.02%.)

L-*Cysteinatodiphenylborane*

M.p. 210°, 41% yield. (Found: C, 63.25; H, 5.67; B, 3.78; N, 4.83; S, 11.30. $C_{15}H_{16}BNO_2S$ calcd.: C, 63.18; H, 5.66; B, 3.79; N, 4.91; S, 11.22%.)

L-*Tyrosinatodiphenylborane*

M.p. 243°, 43% yield. (Found: C, 73.00; H, 5.81; B, 3.24; N, 4.02. $C_{21}H_{20}BNO_3$ calcd.: C, 73.07; H, 5.84; B, 3.13; N, 4.06%.)

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* Melting points were obtained with a Fisher–Johns melting point apparatus and are uncorrected.
** Analyses were performed by Galbraith Microanalytical Laboratory.